Time-dependent behavior of carbon nanotubes and their polymer-based composites under static tension

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**NANYANG
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NANOTUBES AND THEIR POLYMER-BASED
COMPOSITES UNDER STATIC TENSION**

ZHOU ZONGRONG

SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING

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ABSTRACT

This study aims to exploiting the unique mechanical properties of carbon nanotubes (CNTs) for high-performance composite materials at different temperatures through extensive studies on time-dependent behaviors and fracture mechanisms of single-walled carbon nanotube (SWCNT) embedded with different defects, aligned SWCNT bundles at different temperatures and SWCNT bundles/epoxy composites under static tension using experimental methods and molecular level simulations.

Tensile tests of SWCNT ropes consisting of unidirectional, aligned SWCNT bundles were first carried out under constant applied stress at room temperature (23°C). Stress-life (S-N) diagram and creep strain curves of SWCNT bundles were obtained. It is found from the S-N diagram that SWCNT bundles do display fatigue behavior under sustained static tensile load. Compared with static fatigue behaviors of graphite fiber, the fatigue strengths of SWCNT bundle are doubled within 10^4 s and similar at longer times. The fatigue limits of SWCNT bundles seem to exist at 4-5 GPa within the time scale of 48 hours. The creep strain curves obtained experimentally are well fitted by a 4-element Burgers model to verify the validity of the model for characterizing the creep behavior of the SWCNT bundles. The resultant characteristic parameters from the model are obtained and used to plot a creep compliance versus time curve of the SWCNT material at the given temperature. The microscopic observations on fracture surfaces of SWCNT bundles show subsequent fractures occur at a subbundle level, with a characteristic of brittle-like failure, suggesting defect effect and local load shearing mechanism in the failure of SWCNT bundles.

The influence of temperature on creep behaviors of the aligned SWCNT bundles was investigated experimentally. Apart from the room temperature 23°C mentioned above, SWCNT rope samples were tested at 38° and 54°C. Accordingly, the S-N diagrams of SWCNT bundles were obtained and compared with the previous one at 23°C. The fatigue strength of SWCNT bundle at 38°C is about 1.5 times that at 23°C within 10^4 s, and the fatigue limits is estimated to 9 GPa or so within the time scale of investigation, similar to the corresponding value at 54°C. However, the fatigue strength at 54°C is lower within 3400 s and subsequently higher than the corresponding value at 23°C. The creep strain curves of the samples at 38° and 54°C are fitted by the Burgers model, from which the elastic and viscous parameters for the samples are obtained and averaged using the Harmonic Means algorithm. With the elastic and viscous parameters averaged experimentally, creep compliance with logarithmic time curves can be plotted at three given temperatures. It is found that the three compliance curves are similar in shape, taking on a characteristic of obeying time-temperature superposition (TTSP) principle. By horizontal shift along the coordinate axis of logarithmic time, a master curve at a reference temperature of 23°C is generated, which can be applied to predict creep behavior of SWCNT bundles at an arbitrary temperature or long-term creep behavior at lower temperatures to save testing time.

In order to study the effect of defects on the static fatigue life of a SWCNT, a refined life prediction model, taking into consideration carbon-carbon bond rotation and preexisting strain under static tensile loads, is proposed. The time-dependent fracture behaviors of 12 different cases of zigzag (18, 0) SWCNT, each embedded with either a single defect of different types or two interacting or non-interacting defects, are studied under axially applied tensile load. It is shown that the patterns of atomistic crack propagation and fatigue lives of SWCNTs are influenced by the type and/or orientation of the defect(s), inter-defect distance, as

well as the magnitude of externally applied stress. For SWCNTs with two defects, if the inter-defect distance is within certain a length, defect-defect interaction does exist and it has pronounced effects on diminishing the lives of the nanotubes. Also, the defect-defect interaction is stronger at shorter inter-defect distance, resulting in shorter fatigue lives.

Static fatigue tests of epoxy composite embedded with SWCNT rope were carried out on an Instron 8800 micro-force tester with a static load cell with a capacity of 100 N. Neat epoxy samples were also tested and compared with the results obtained for the composite. The creep behaviors of both neat epoxy and the composite obtained experimentally can be modeled by the 4-element Burgers model, and the corresponding elastic and viscous parameters are obtained. Using the characteristic elastic and viscous parameters for the SWCNT and neat epoxy, the characteristic elastic and viscous parameters for SWCNT/epoxy composite are deduced based on the ratio of the SWCNT bundle and the epoxy in the composite. The predicted creep behavior of the SWCNT/epoxy composite is in very good agreement with experimental results. Time-to-failure of SWCNTs in SWCNT/epoxy composite is similar to that of the stand-alone SWCNT (or say SWCNT in bundle) at higher applied stresses. However, at lower applied stresses, time-to-failure of the SWCNTs in the composite is longer. This is believed to be attributed to load transfer from the epoxy matrix to the SWCNT bundles in the composite, and the fact that the stand-alone SWCNT are under increasing stress under long-term static fatigue load when subbundle failures have occurred. The fracture morphologies of SWCNT/epoxy composites suggest that fatigue fracture mechanism of the composite include epoxy matrix cracking, splitting and fracture of SWCNT bundles and pullout of SWCNT bundles from the epoxy.

NOMENCLATURE

Symbol	Description
a	Length of unit vector of CNT
$\mathbf{a}_1, \mathbf{a}_2$	Unit vectors of CNT
$\mathbf{R}$	Chiral vector of CNT
L	Circumference of CNT, i.e. length of $\mathbf{R}$
d	Diameter of CNT
θ	Chiral angel of CNT
r	Radius of CNT
h	Half of the gap between two adjacent SWCNTs
ε	Strain
σ	Applied stress
T	Temperature
T_r	Reference temperature
Q	Activation energy for creep
B	Reciprocal factor of frequency
J	Creep compliance
R	Universal gas constant

E	The highest bond energy
D	Inter-defect distance in a SWCNT
ξ_i	The total strain energy per atom C-C bond
U_0	Dissociation energy
u_i	Strain energy associated with the i th mode crack front C-C bond
γ_i	Coefficient of strain energy concentration
τ_0	Reciprocal of the fluctuation frequency of atoms
k	Boltzmann constant,
i	Denotes the C-C bonds to be broken
t_i	Lifetime of each individual C-C bond around its circumference
t	Lifetime of a CNT
CNT	Carbon nanotube
CVD	Chemical vapor deposition
FESEM	Field emission scanning electronic microscopy
HiPCO	High pressure carbon monoxide
HRSEM	High-resolution scanning electron microscopy
MMTD	Micro-mechanical testing device
MWCNT	Multi-walled carbon nanotube
SEM	Scanning electronic microscopy
SWCNT	Single-walled carbon nanotube

SW defect	Stone-Wales defect
TEM	Transmission electron microscopy
TTSP	Time-temperature superposition
WLF	Williams-Landel-Ferry

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CHAPTER 1

INTRODUCTION

1.1 Background and significance

Carbon nanotubes (CNTs) have been the focus of tremendous research for more than two decades because of their electrical, thermal, and extraordinary mechanical properties. Numerous studies have shown that single-walled carbon nanotubes (SWCNTs) have very high current carrying capacity and axial thermal conductivity, which make them an attractive electronic, sensing, or heat sinking material for nano-electromechanical systems (NEMS) and integrated circuitry in future [1-4]. More importantly, SWCNTs possess unique mechanical properties, such as exceptionally high Young's modulus (~ 1.8 TPa), very high axial tensile strength (~ 30 GPa) with excellent flexibility and resilience [5-8], and excellent creep and fatigue resistance [9, 10]. The exceptional mechanical properties of CNTs, coupled with their low density (~ 1.3 - 1.4 g/cm³), imply that CNTs have the potential to become candidates for reinforcement for high performance composites for structural applications [11-13].

A great deal of experimental and theoretical studies concerning the mechanical behaviors of CNTs have been reported in the past decade or so. Experimentally, the Young's moduli of isolated SWCNTs and SWCNT ropes, in the terapascal range, were estimated by measuring the amplitude of intrinsic thermal vibrations in the transmission electron microscope (TEM) and directly measured with a "nanostressing stage" located within a scanning electron microscope (SEM), respectively [14-16]. Theoretically, elastic properties of SWCNTs and

multi-walled carbon nanotubes (MWCNTs) were studied using an empirical force constant model and tensile Young's modulus (~ 1 TPa), torsion shear modulus (~ 0.5 TPa), and bulk modulus (~ 0.2 TPa) of tubes were offered, suggesting that CNTs possess high elastic stiffness [17-19].

However, macroscopical SWCNTs are commonly in bundles or ropes. A bundle can contain up to several hundred SWCNTs, well arranged in a hexagonal lattice by Van der Waals force [20]. Large collections of well-aligned SWCNT bundles form a SWCNT rope. The mechanical properties of the SWCNT bundle or rope are usually influenced by not only length, diameter, chirality and boundary conditions of single SWCNTs involved [21, 22], but also by configurations of these SWCNTs (straight or curved) [23], overlap and spacing at the tube-tube junctions, and the number of SWCNTs in the bundle or rope [24, 25]. As a result, their mechanical properties are diffused and far inferior to theoretical predictions, which might be attributed to poor inter-tube interaction to some extent. Since the Van der Waals force that binds the tubes within a CNT bundle or rope together is weak, the nanotubes easily slide on each other, giving rise to lower mechanical properties for larger bundles compared with individual SWCNTs. The highest Young's modulus for macroscopic CNT bundles produced so far is mere 80 GPa and the bending modulus of CNT bundles, which is equivalent to the Young's modulus for the homogeneous CNT bundles, strongly decreases with the diameter of bundles [20, 26, 27]. Therefore, owing to weak intertube forces, thick bundles behave as loose bundles of individual tubes that can easily slide past each other, rather than as a thick bar, which do not take full advantage of the superior mechanical properties of CNTs.

Some researchers have made efforts for investigation and improvement on mechanical properties of CNT fiber and CNT-polymer nanocomposites [28-33].

CNT fiber can be spun directly and continuously from an aerogel of double-walled carbon nanotubes and its mechanical property is regulated by the winding rate of drawing the aerogel [28]. Other techniques, such as spinnings from a lyotropic liquid crystalline suspension and MWCNTs previously grown on a substrate as semi-aligned carpets, can also be used to produce CNT fibers [29, 30]. Different techniques produced different CNT fibers in their mechanical properties, such as strength or stiffness. For CNT fiber spun directly, the highest strength and stiffness reported were 2.2 GPa and 160 GPa [31]. Interfacial sliding of nanotube fibers within a polymer or epoxy matrix was studied and the tube-matrix sliding energy dissipation mechanism was explored in CNT reinforced composites [32]. Multilayered 3D composites with nanotube forests were fabricated, which improved remarkably interlaminar fracture toughness, hardness, delamination resistance, in-plane mechanical properties and damping [33]. Besides, influences of environmental temperature on the mechanical properties of CNTs and their composites have also been reported [34-40].

Despite these tremendous efforts, our understanding of the mechanical behaviors of CNTs and CNT-based composites are not yet comprehensive. Most studies are concerned with transient loading and few are under prolonged loading. Very limited research concerning time-dependent fracture behaviors and mechanisms of CNTs and CNT-based composites has been reported so far.

Only a few reports on time-dependent behaviour of CNTs are seen [9, 41, 42]. An experimental study on static and dynamic fatigue behavior of aligned SWCNT bundles under tension was performed and static and dynamic fatigue strengths of the CNT bundles were obtained. Compared with corresponding fatigue strength of graphite fiber, static fatigue strength of CNT bundles was at least double within 10^4 seconds and similar at longer time, and dynamic fatigue strength was

twice within up to 10^7 cycles [41]. Theoretically, time-dependent failure behavior of a zigzag type SWCNT under constant tensile load was characterized by molecular modeling and the logarithm of time-to-failure of CNT was predicted to be approximately linearly related to applied stress [42]. Based on the molecular simulation, the obtained time-to-failure of SWCNTs with defects compared with experimental results, suggesting defect deteriorative effect on fatigue behavior of SWCNTs. Mechanical response of aligned nanotube arrays under compressive cyclic loading was investigated and it was found that the nanotube arrays possessed the characteristics of preconditioning, viscoelasticity-induced hysteresis, nonlinear elasticity, stress relaxation and large deformation, and that no fatigue failure was observed even at high strain amplitudes up to 5×10^5 cycles [9]. All these efforts indicate that CNT has good creep and fatigue resistance and its fatigue behavior may be affected by defects.

Fatigue and creep behaviors of CNT polymer-based composites under different loading modes have been investigated. Fatigue behavior of CNT reinforced epoxy composite under tension-tension dynamical loading was studied, fatigue fracture surface of samples was analysed and fracture mechanisms were revealed [43-45]. Fatigue life of glass fiber/polymer composites with MWCNTs under dynamic loading was studied [46]. The results showed that the incorporation of small content of MWCNTs can significantly improve high-cycle fatigue life of the matrix. Creep compliance of polypropylene/MWCNTs composites increased with increasing temperature. Moreover, using a time-temperature superposition (TTSP) principle based on the William-Landel-Ferry (WLF) equation [47], a master curve of creep compliance at an arbitrary relatively low temperature was constructed, by which the long-term creep behavior of the composites could be predicted at the temperature. All these efforts indicate that the assembly of CNTs possess excellent fatigue and creep resistances at ambient temperatures and creep

property of CNT/polymer composites would be affected by environmental temperature.

Despite these efforts, however, some questions, such as how temperature influences creep behavior of CNTs, how defects affect static fatigue life of CNTs, and fracture mechanism of CNTs and their composites under static tension have been receiving less attention.

Time-dependent mechanical failure resulting from creep is the most common cause of service failure in long-term loading engineering structures and it may occur under loading conditions where the applied stress is below the tensile strength and even below the elastic limit [48]. In general, the process of creep is divided into three successive stages according to the stability of the strain rate: initial stage (primary creep), secondary stage (steady-state creep) and tertiary creep. In the initial stage, the strain rate starts with a relatively high value, gradually slows down and eventually reaches a minimum. In the steady-state stage, the strain rate is still stable, keeping near constant at the minimum, which is so called characterized creep strain rate and often used as a design parameter. In the tertiary creep, the strain rate exponentially increases with strain, because of necking phenomena. The mechanisms of fatigue have been established for conventional engineering materials, such as metals, ceramics, and conventional fiber composites. However, our understanding on creep behaviours and fatigue mechanisms of CNTs and their composites is still very limited.

In order to gain a comprehensive understanding on long-term behavior of CNTs and CNT-based composites and to unlock the potential load-bearing, structural applications of CNTs for advanced composites, a fundamental study of time-dependent behaviors of SWCNT bundles and SWCNT/epoxy composites

under static tension is performed in this study. Particularly, emphasis is placed on the influences of temperature and defects on time-dependent behaviors of SWCNT bundle under static tension.

1.2 Overall objectives and specific aims

The objective of this work is to exploit the unique mechanical properties of CNTs toward the development of high-performance composite materials through studying time-dependent behaviors and fracture mechanisms of CNTs and their composites under static tension. This is realized by both experimental studies and molecular level simulations. Specific aims are as follows:

- (i) To study time-dependent behavior of SWCNT bundles under static tensile load at room temperature.
- (ii) To study time-dependent behavior of SWCNT bundles under static tensile load at different temperatures, showing influence of temperature on creep behaviors of CNTs.
- (iii) To apply TTSP principle to study creep behavior of SWCNT bundles under static tension at three temperatures to generate a master curve, which can be applied to predict creep behavior of SWCNT bundles at an arbitrary temperature or long-term creep behavior at lower temperatures.
- (iv) To predict time-dependent behavior of defective SWCNTs using molecular simulation, showing how defects and defect-defect interaction affect the fatigue behavior of SWCNTs and revealing the fatigue mechanism of SWCNTs at the atomistic scale.

- (v) To study experimentally and analytically time-dependent behaviors and the failure mechanism of the SWCNT rope reinforced composites.

1.3 Organization

This thesis is organized into seven chapters. The background, significance, overall objective, specific aims and organization of the study are introduced in Chapter 1. Current status of research on time-dependent behaviors of CNTs and their composites and the effects of defect and temperature, as well as basic knowledge and synthesis of CNTs and their composites, are briefly reviewed in Chapter 2. A study of time-dependent behaviors of SWCNT bundles under static tension is presented in Chapter 3, where stress-life (S-N) diagram is plotted, creep behavior is characterized analytically by a 4-element model, and the fracture morphology and mechanisms are investigated through field emission scanning electronic microscopy (FESEM) observations. In Chapter 4, the influence of temperature on creep behavior of SWCNT bundle is investigated and the TTSP principle is applied to creep compliance of SWCNT bundle to predict creep behavior of SWCNT bundle at an arbitrary temperature. In Chapter 5, molecular simulations are used to study time-dependent behaviors of SWCNTs with different defects on the basis of the classical kinetic concept of solid fracture and a strain concentration concept, to reveal the effect of defect interaction on static tensile fatigue behavior of SWCNTs. In Chapter 6, we study time-dependent behaviors of SWCNT rope/epoxy composites experimentally and analytically, to offer theoretic guidance for designing different SWCNT composite to meet the requirement of creep. Finally, conclusions and future work are outlined in Chapter 7.

CHAPTER 2

LITERATURE REVIEW

In this chapter, researches on the time-dependent mechanical behavior of CNTs and their composites and the effect of temperature and defects on the mechanical behavior of CNTs, as well as the structure and synthesis of CNTs and processing of CNT reinforced composites, are reviewed. First, the structure of a CNT is described. Next, synthesis techniques for the CNTs and the processing of CNT reinforced composites are briefly described. Lastly and most importantly, critical issues associated with long term behaviors of CNTs and their composites, and the effect of temperature and defects on the long term behaviors are reviewed.

2.1 Structure of CNT

CNTs can usually be divided into two groups: SWCNTs and MWCNTs. The structure of a SWCNT is basically viewed as a rolled up sheet of graphene, shown in Fig. 2.1. Graphene is a one-atom-thick planar sheet of carbon atoms that are densely packed in a crystalline hexagonal structure held together by strong covalent bonds. This makes SWCNT bundles always remain crystalline without a glass transition. However, MWCNTs consist of several concentric SWCNTs, each cylinder being a SWCNT with the spacing between the adjacent layers of around 0.34 nm, close to the interlayer spacing of graphene in graphite (0.335 nm) [49]. These concentric SWCNTs are held together primarily by Van der Waals forces, which are relatively weak compared to covalent bonds. As in the case of graphene, each carbon atom in SWCNTs is held in a hexagonal crystal lattice by covalent bonds, in addition to Van der Waals force in interlayer interactions for

MWCNTs.

Fig. 2.1 Schematic formation of (a) a carbon nanotube rolled from (b) a hexagonal graphene sheet.

The structure of a CNT is uniquely described by its chirality (the manner a sheet of graphene is “rolled” into a tube). Based on the chiral vector (n, m) , CNTs are classified as zigzag, armchair and chiral tubes, where n and m are integers of the chiral vector $\mathbf{R} = n\mathbf{a}_1 + m\mathbf{a}_2$ in the graphene plane, as shown in Fig. 2.1(b), in which the two unit vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ are shown. The vector $\mathbf{a}_1$ lies along the zigzag line. The wrapping angle θ is formed between $\mathbf{R}$ and the zigzag line. If $\mathbf{R}$ 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 $0^\circ < \theta < 30^\circ$, it is a "chiral" tube. The three types of tubes are shown in Fig. 2.2 (a), (b), and (c), respectively. It is seen from Fig. 2.1(b) that the length of unit vectors, a , is $\sqrt{3}$ times the length of carbon-carbon bond, which is 0.142 nm. Since the chiral vector $\mathbf{R} = n\mathbf{a}_1 + m\mathbf{a}_2$, spans the circumference of a nanotube, one can calculate

the nanotube circumference, L , diameter, d , and the chiral angle, θ , from the (n, m) indices. These typical parameters are summarized in Table 2.1 [50].

Fig. 2.2 Schematic diagram of atomic structures for three types of SWCNTs: (a) armchair, (b) zigzag and (c) chiral. Spheres represent carbon atoms and the sticks connecting the spheres represent carbon-carbon bonds.

Table 2.1 Parameters of carbon nanotubes [50].

Symbol	Name	Formula	Value
a	Length of unit vector	$a = \sqrt{3}a_{C-C} = 0.246 \text{ nm}$	$a_{C-C}=0.142 \text{ nm}$
$\mathbf{R}$	Chiral vector	$\mathbf{R} = n\mathbf{a}_1 + m\mathbf{a}_2 \equiv (n, m)$	$0 \leq m \leq n$
L	Length of $\mathbf{R}$	$L = \mathbf{R} = a\sqrt{n^2 + m^2 + nm}$	
d	Diameter	$d = L/\pi$	
θ	Chiral angle	$\sin \theta = \frac{\sqrt{3}m}{2\sqrt{n^2 + m^2 + nm}}$ $\cos \theta = \frac{2n + m}{2\sqrt{n^2 + m^2 + nm}}$	$0 \leq \theta \leq 30^\circ$ $\tan \theta = \frac{\sqrt{3}m}{2n + m}$

The CNTs mentioned above are perfect nanostructures without defects. As more

experimental observations and theoretical studies became available, CNTs are found to be not as perfect as they seem but embedded with some defects. The defects can be classified into four categories: topological (introduction of ring sizes other than hexagons), rehybridization (ability of carbon atom to hybridize between sp^2 and sp^3), and incomplete bonding defects (vacancies, dislocations, etc.) and doping with other elements than carbon [51]. Of these defects, Stone-Wales (SW) defect [52] (topological defect) is one of the most commonly observed defects. It is a pentagon-heptagon pair and its formation can be viewed as a 90° rotation of a sp^2 bond, i.e., so-called SW rotation, as indicated in Fig. 2.3. The SW defect and its formation mechanism have a strong influence on ductility, ultimate strength, and fracture modes of CNTs [53]. Influences of the defects on the time-dependent mechanical behaviors of CNTs will be addressed in detail in Section 2.3.

Fig. 2.3 Schematic formation of a pentagon-heptagon pair Stone-Wales (SW) defect by a 90° rotation of a sp^2 bond as indicated by a thick line. The formation formally requires two sigma bonds shown to be broken and two new bonds to be formed as indicated by the arrows.

2.2 Synthesis of CNT and processing of CNT reinforced composites

Carbon nanotubes are synthesized using a wide variety of different techniques, such as arc discharge [54-58], laser ablation [59-62], high pressure carbon

monoxide (HiPCO) [63, 64], and chemical vapor deposition (CVD) [65-69]. Both arc discharge and laser ablation present limitations to the large scale production. Most of these processes take place in vacuum or with process gases. However, the gas-phase methods (catalytic growth from HiPCO and CVD) replace continuously the carbon source (gas), allowing continuous processing of CNTs. Large quantities of nanotubes can be synthesized by these methods, which make CNTs more commercially feasible with more advances in catalysis and continuous growth processes. However, as more experimental observations and theoretical studies became available, CNTs produced were found to be not as perfect as they seem, and their exact mechanical properties are considerably inferior to theoretical values [5, 27].

CNT used in this study was synthesized by a novel floating catalyst approach in which benzene was catalytically pyrolyzed at 1100-1200 °C on a large scale at low cost [70]. The as-synthesized products consist primarily of long ropes of aligned SWCNT bundles with rope diameters of about 100 μm and lengths of about 20~40 mm. Microscopically, the ropes of aligned SWCNT bundles consist of many roughly-aligned bundles with approximately constant diameter ranging from 10 to 40 nm. The bundles consist of well-arranged SWCNTs with tube diameter of about 1.4-2 nm in a hexagonal crystal lattice [70, 71]. The ropes of aligned SWCNT bundles are easily handled and manipulated by hand or simple tools. For instance, the ropes can be roughly separated, stretched and incorporated into epoxy resin matrix to form a mini-composite structure for conventional mechanical testing. Besides, they can also be separated into very thin SWCNT ropes with 1.5-3 mm in length and 5~20 μm in width or diameter using tweezers for micro-mechanical testing in this study.

Several different techniques of embedding CNTs into a polymer matrix to form a

film have been developed, including the most effective solution-evaporation methods with sonication and calendering [72, 73]. In the sonication method, sonication of nanotubes in a solvent is used and later a polymer is added to the solution. Once the nanotubes are dispersed by sonication, the solution is introduced into a mold and cured at room temperature [72]. The nanotubes are manually mixed into the polymer and dispersed using a two- or three-roll calendar in the calendering method. The film obtained is subsequently cured at room temperature and post-cured at a temperature of about 60°C, depending on the polymer matrix used in the experiment [26, 74]. The mechanical properties of the CNT composites generated are often worse than expected due to various influences, which hinders the application of CNTs as a reinforcement.

At present, the processing of CNT reinforced composites has been a major challenge to extensive application of CNTs as a reinforcement. In the fabrication process, the most important technical problems are how to achieve the following four aspects: (1) good dispersion of the CNTs in the polymer matrix [73], (2) good alignment of these CNTs in the direction of the load [72, 75, 76], (3) good adhesion between the nanotubes and the matrix [21, 77-85], and (4) appropriate quality/quantity of CNTs embedded, since they influence the mechanical properties of the final composites. Actually, it is very important to control the maximum volume (or weight) fraction of CNTs in the matrix in the manufacturing process, since no further improvements in mechanical properties of the composite are achieved when the volume fraction of CNTs in a composite is beyond certain value [86]. Moreover, as volume fraction of CNTs is higher, dispersion and alignment deteriorate, voids and CNT agglomerates easily form, leading to a reduction of mechanical properties of composites. Therefore, it is critical to achieve good dispersion, alignment, and adhesion of CNTs in the matrix in order to take full advantage of the wonderful mechanical properties of the CNTs.

2.3 Time-dependent mechanical behavior of CNTs and their composites

As mentioned in Chapter 1, only a few studies on time-dependent behaviors of CNTs and CNT-based composites are available. Here, we briefly review the studies on fatigue behavior and creep behavior of CNTs and their composites.

2.3.1 Fatigue behavior

Experimental and theoretical studies on fatigue behavior of CNTs and their composites were also reported, mainly from Liao's group [41-44, 87, 88] and several other groups in recent years [45, 89].

In Liao's group, fatigue behavior of aligned SWCNT reinforced epoxy composite under tension-tension cycled loading was investigated experimentally [43]. The relationship obtained between applied cyclic stress and logarithm of time-to-failure for SWCNT/epoxy composites is demonstrated by an S-N curve that is similar to that of carbon/epoxy composites, although SWCNTs within the composite is loaded at much higher cyclic stresses. The results show that the SWCNT ropes are good reinforcement in polymer-based composites because of their high fatigue resistance and fracture toughness.

Subsequently, fatigue failure mechanism of SWCNT/epoxy composites under repeated tensile load was studied using a combination of experimental methods and molecular mechanics simulations [44]. Experimental observations by TEM showed failure modes included splitting of SWCNT bundles, kink formation and subsequent failure in SWCNTs and fracture of SWCNT bundles. The results of molecular mechanics simulation reasonably well reproduce fracture surface of

SWCNT observed experimentally, suggesting that SW defects might be a factor of fatigue failure mechanism of SWCNT/epoxy composites.

On the other hand, time-dependent failure of a zigzag type SWCNT under tensile load was characterized theoretically by Xiao *et al.*[42]. A model was proposed for predicting time-dependent fracture of a defect-free zigzag SWCNT under low applied strain, using Zurkov's concept of dynamic fracture [90]. When a SWCNT is subjected to tensile load, the bond at the crack front was considered parallel to the direction of nanotube tensile deformation (the longitude direction), shown in Fig. 2.4. Accordingly, the lifetime, t , of the tube, is the summation of the lifetime, t_i , of each individual C-C bond to be broken:

$$t = \sum_i t_i = \sum_i \tau_0 \exp\left(\frac{U_0 - u_i}{kT}\right) = \sum_i \tau_0 \exp\left(\frac{U_0 - \gamma_i \sigma^2}{kT}\right) \quad (2.1)$$

where i represents number of the C-C bonds to be broken. In Eq. (2.1), U_0 is the C-C bond dissociation energy and taken as 1.84×10^{-19} J/m², u_i represents the strain energy of the single C-C bond to be broken, σ is nominal stress on the SWCNT, τ_0 is the reciprocal of the fluctuation frequency of atoms and taken as 10^{-13} s, k is the Boltzmann constant and taken as 1.38×10^{-23} J/K, and the absolute temperature T is 300 K. γ_i is a crucial term related to "crack-tip" strain energy concentration and calculated using molecular simulations. γ_i is the only indispensable parameter required in calculating fatigue life of a SWCNT, and it needs to be evaluated again for the new atomic crack geometry after a C-C bond has been broken. Using the model, fatigue behavior of a SWCNT with a single SW defect was also studied [91]. It was found that a defective SWCNT had lower static fatigue strength and shorter static fatigue life compared to a defect-free nanotube of the same type.

Fig. 2.4 Schematic diagram of cracking modes of a zigzag carbon nanotube. The single C-C bonds to be broken are indicated by red thick lines. The number of the bonds are denoted by i and their strain energies are represented by u_i [42].

Recently, Ma *et al.* [41] studied static fatigue behavior of aligned SWCNT bundles under tension at room temperature using a nano-mechanical tester. It was found that SWCNT rope displayed a typical viscoelastic behavior with primary, steady state, and tertiary regions and the S-N diagram has two distinct regions: a plateau region where static fatigue strengths are relatively high and fatigue lives are short, followed by a region with decreasing static fatigue strength and longer fatigue life. Further analysis showed that the static fatigue strengths of SWCNT bundles were more than twice that of graphite fiber within 10^4 seconds and fatigue limit was about 4 GPa within a time scale of 48 hours. Coupled with fatigue life of a defective SWCNT obtained by molecular modeling, it was suggested that defects have deteriorative effects on the static fatigue behavior of SWCNTs.

Even though how defects and defect-defect interaction influence the fatigue behavior of a CNT is still unclear, preliminary probe into defect-defect interactions within a SWCNT has been reported [87, 88]. Using molecular mechanics simulations, Huq *et al.* [87] have quantified interactions of SW defects in a SWCNT by the magnitude of the potential energy of the C-C bonds, E . A “weak”

bond is the one with highest potential energy and is more prone to rupture than its neighboring bonds. They have also pointed out that the degree of defect-defect interactions depends on defect type, inter-defect distance, D , and orientation of defects. Moreover, they also analyzed the interactions between a pair of SW defects in a SWCNT subjected to an external torque, pointing out that the magnitude of E depends on the type of defect but the profile of the E versus D curve depends on the orientation of the defects.

A few findings on fatigue behavior of CNTs and their composites from other groups have been reported more recently. Suhr *et al.* [9] investigated mechanical response of aligned nanotube arrays under compressive cyclic loading and found that such nanotube arrays possessed the characteristics of preconditioning, viscoelasticity-induced hysteresis, nonlinear elasticity, stress relaxation and large deformation, and that no fatigue failure was observed at high strain amplitudes up to 5×10^5 cycles, which suggested wide applications of nanotubes in tissues engineering repair and compliant electrical contacts.

Fatigue behaviors of various CNT composites under different loading modes have been investigated. Zhang *et al.* [45] studied tensile fatigue behavior of CNT/epoxy composites when an initial pre-crack was created in the samples. The embedded CNTs were either SWCNTs with a mean diameter of 1.5 nm and length of 20 μm or MWCNTs with a mean diameter of 20 nm and length of 20 μm . They were both very pure with the purity of up to 95%. Fatigue test results showed that crack propagation rate was reduced by an order of magnitude for an epoxy resin system with an addition of ~ 0.5 wt.% of CNT additives and the degree of the decrease became more significant with the increase of diameter and length of nanotubes and the improvement of nanotube dispersion. The cause of crack suppression was revealed by the microscopic observations and fracture mechanics

modeling, which was due to an effective crack-closing stress when nanotube fibers were pulled out in the wake of the crack tip.

Grimmer *et al.* [46] studied fatigue life of glass fiber/polymer composites with MWCNTs mixed in the polymer matrix under dynamic loading. The results show that the addition of small volume fractions of MWCNTs can significantly improve high-cycle fatigue life of the matrix. Moreover, an energy-based model was proposed to estimate the additional strain energy absorbed in fatigue in view of the mechanism of improved fatigue life that the fracture and pull-out of nanotubes will absorb some energy by bridging across nano-scale cracks and from the matrix.

Fatigue delamination of the matrix of glass fiber/polymer composites with CNTs was also studied [92]. It was found that the incorporation of small volume fraction of MWCNTs into the matrix can significantly reduce cyclic propagation rate of delamination crack and increase critical and sub-critical inter-laminar fracture toughness values. Through high-resolution scanning electron microscopy (HRSEM) observation of the fracture surfaces, the CNTs were found to be at the delamination crack front, which was able to slow the propagation of the crack due to fracture, pull-out of the nanotubes, and bridging of crack. The increased inter-laminar fracture resistance for the CNT-embedded composite was presented at lower levels of applied cyclic strain energy release rate. By fracture mechanics analysis and comparison with experimental results, it was revealed that fracture behavior of the CNTs played a crucial role in the associated increase in the fracture resistance compared with that of the composites not containing CNTs.

2.3.2 Creep behavior

The creep behaviors of CNTs and their polymer-based composites have been

investigated under different loading modes (tensile or compressive). Creep behavior of vertically aligned carbon nanotube arrays was studied through nanoindentation experiments [93]. Instantaneous control stress and strain rate were recorded and creep strain rate sensitivity of the CNT array was calculated. It was found that the creep behavior was related to the density of the vertically aligned CNT arrays. No more research on creep behavior of pure CNTs has been reported so far. However, there are some studies on creep behavior of CNTs composites.

Zhang *et al.* [94] studied the tensile creep behavior of SWCNT/epoxy composites under a constant load. It was found that SWCNTs were effective in inhibiting creep deformation of polymeric structure and only 0.1-0.25 wt% of SWCNT additives can significantly reduce the creep deformation. More content of SWCNT of about 1 wt% caused creep performance to deteriorate rapidly due to ineffective dispersion of SWCNTs in the epoxy matrix. However, in the range of 0-0.1 wt%, an increase of nanotubes brought about better creep resistance. Moreover, increasing the applied stress significantly reduced the ability of SWCNTs additives to modulate the creep strain of the nanocomposites. Therefore, nanotube additives could be the key enabler for the long-term higher-temperature application of polymeric structures which would otherwise fail by excessive creep deformation.

The creep behaviors of MWCNT/polypropylene composites were studied through short term tensile creep tests [47, 95]. It was found that the creep strain increased as temperature increased and the content of CNTs was reduced. The added CNTs improved the recovery property of the composites remarkably, especially at high temperature. The plastic creep strain of the composites decreased by 53% compared to that of neat polymer matrix when volume fraction of CNTs is only 1%.

Meanwhile, a 4-element Burgers model was employed to characterize the creep curves and the contribution of each Burgers element to the total deformation was calculated. Since creep tests of the nanocomposites had been carried out at different temperature and corresponding creep curves had been obtained, all the creep curves obtained were shifted along the log (time) axis and superposed to generate a master curve. The shift factor obeys the Williams-Landel-Ferry (WLF) equation when all temperatures are above glass-transition temperature of the composites. This confirms the creep behavior of MWCNT/polypropylene composites obeys the time-temperature superposition (TTSP) principle, which is usually applied to predict the long-term creep behavior of the composites.

2.4 Summary

A brief review has been presented on the time-dependent mechanical properties of CNTs and their composites. The incorporation of CNTs had improved the creep recovery property of the composites remarkably, especially at high temperatures. The 4-element Burgers model had been employed to characterize the creep behaviors of the CNT composites. The influence of temperature on creep property of CNT composites has also been presented. TTSP principle had been employed to predict the long-term behavior of the CNT composites via a master curve generated from the superposition of all test curves at different temperatures. Results of static and dynamic fatigue tests indicate that CNTs are good reinforcement material in polymer-based composites because of excellent fatigue resistance and high fracture toughness of CNTs. The incorporation of CNTs in composites improved the fatigue life of the matrix, which was attributed to the absorption of energy existing in both the fracture of CNTs bridging across nano-scale cracks and the pull-out of CNTs from the matrix. Existence of defects

in a SWCNT will shorten static fatigue lifetime of the SWCNT.

Despite these efforts, no systematic studies of the creep and fatigue behaviors of CNTs and their composites under static tension are available in the literature. For the present study, we aim at a fundamental understanding of the following points: (i) time-dependent behavior of CNT bundle at room temperature; (ii) effect of temperature on time-dependent behavior of CNT bundle; (iii) how do inter-defect interactions affect time-dependent fracture behavior of a SWCNT; and (iv) time-dependent behavior and failure mechanism of CNT reinforced composites.

CHAPTER 3

TIME-DEPENDENT BEHAVIOR OF SWCNT BUNDLE UNDER STATIC TENSION AT ROOM TEMPERATURE

As mentioned in Section 2.3.1, stress-life (S-N) diagram of SWCNT bundle displayed typical fatigue behavior with decreasing strength and longer fatigue life under sustained static tensile load. Compared with graphite fiber, the fatigue strength of SWCNT bundle was doubled within 10^4 s and similar at longer times. The fatigue limits of SWCNT bundles seemed to exist at 4-5 GPa within the time scale of 48 hours. Moreover, creep behaviors of various CNT/epoxy composites were characterized by a 4-element Burgers model, usually used for describing viscoelastic behavior of many materials in creep. However, no systematic study of time-dependent behavior of CNT bundle has been performed, and little is known about failure mechanism of CNT bundle in creep.

In this chapter, we present the results of a systematic study on time-dependent behavior of CNT bundle under static tension at room temperature. Creep strain vs. time curves and S-N diagram are combined to better characterize the time-dependent behaviors of samples under static tension. The 4-element Burgers model is elaborated and adopted to formulate the relationship between creep strain and time. Based on the formulation of the 4-element model, strain vs. time curves obtained from creep tests are analyzed for each sample, which is helpful for understanding creep behavior of CNT bundle and revealing its creep mechanisms. The S-N diagram show characteristics of static fatigue of SWCNT bundle. Morphologies of fracture surface of SWCNT rope are finally observed by FESEM to reveal the creep mechanisms, which can be compared with the result

analyzed by the Burgers model.

3.1 Experiments

Twenty-nine specimens of SWCNT ropes, so-called aligned SWCNT bundles, are successfully tested at room temperature (in which failure occurred within the “grip region”) on a micro-mechanical testing device developed in-house. Load applications include two phases: initial quasi-static ramp, followed by a constant load hold. Force-displacement-time data are recorded in real time.

3.1.1 Material and specimen

The material used for creep test is SWCNT rope, synthesized by a catalytic pyrolysis of hydrocarbons by Cheng *et al.* [70]. The as-synthesized SWCNT ropes are many collections of aligned SWCNT bundles and even up to 100 mm long, as shown in Fig. 3.1 (a). The diameters of these bundles are constants over their entire lengths and different for different bundles, ranged from tens of micrometers to 100 μm . This is attributed to the fact that SWCNTs in a bundle are arranged in a two-dimensional hexagonal lattice and each bundle contains a different number of SWCNTs. The Gaussian mean diameter of individual SWCNTs is 1.69 nm [71]. By carefully separating the SWCNT rope with tweezers, some smaller SWCNT ropes can be split out as test samples. In order to ensure sufficient supply of samples (a sample may be damaged or lost during mounting), test samples are well prepared and allowed to be scattered on the bottom surface of a container, indicated with arrows in Fig. 3.1 (b). Each SWCNT rope specimen consists of some aligned SWCNT bundles, with the length within grip region of about 1.5-3 mm and the diameter or width of 1-20 μm measured from CCD images.

However, because of the irregularity of cross section and the existence of spacing between CNT bundles in a SWCNT rope, it is very difficult to directly measure the final effective cross-sectional area of a CNT rope sample. In the study, we reversely calculate the effective cross-sectional area by using a force-deformation curve at elastic stage obtained experimentally and an estimated Young's modulus of SWCNT bundle. Detailed calculations will be described in Section 3.2.

Fig. 3.1 Photos of (a) as-synthesized SWCNT rope and (b) test samples of small SWCNT ropes to be separated from it. Arrows indicate small SWCNT ropes.

3.1.2 Experimental setup

The testing device, micro-mechanical testing device (MMTD), consists of three main parts: a force transducer, a motion control unit, and a side view visualization unit, shown schematically in Fig. 3.2. The transducer is used to measure loads applied along the axial direction of a bottom output loading tip. In view of the small size of the SWCNT rope, a transducer with maximum force capability of 0.01 N and a resolution of 0.2 μ N was selected (Model 405A, Aurora Scientific Inc., Canada). The loading tip of the transducer is a thin borosilicate glass tube, with outer and inner diameters, and length, of 1.0, 0.5, and 10 mm, respectively.

Fig. 3.2 Schematics of the micromechanical tester device (MMTD): (A) loading tip, (B) force transducer, (C) displacement motor, (D) data acquisition and control unit, (E) lens/CCD camera, (F) copper cylinder, (G) riser, (H) SWCNT rope, (I) glue.

The motion control unit is tightly attached to the upper surface of the force transducer and used to measure and control the position of the loading tip, of which the main part is a DC motor with a travel range of up to 10 mm and a

resolution of 0.05 μm (M-227.10, Physik Instrumente, German).

The side view visualization unit is used for mounting sample, capturing test process, and taking high magnification images for post test analysis, composed of a long focal distance objective lens incorporated with a computer-linked CCD camera. Test control and data acquisition are achieved via an interactive software system based on the LabVIEW platform.

Sample mounting position in the MMTD can be seen from Fig. 3.3 (a). In the figure, a force transducer and its loading tip, lens, and a 12 mm-diameter, 5 mm-high copper cylinder as a fixed stage on a riser are labelled, respectively. Samples are adhered between the loading tip and the bottom copper pad via a glue (Alteco #110 Super Glue, Alteco Chemical PTE LTD), indicated by a circle. The close-up of the locality is shown in Fig. 3.3 (b) - (d), from which the procedures for specimen mounting are demonstrated. The procedure is described as follows: (i) to add a drop of glue onto the loading tip below the force transducer (see Fig. 3.3 (b)); (ii) to adhere a selected SWCNT rope to the loading tip (see Fig. 3.3 (c)). It is noted that the selected SWCNT rope should be placed in advance on the tip of tweezers in a manner that the SWCNT rope can be easily detached themselves from the tweezers; (iii) to add a drop of glue on the surface of a copper cylinder and place the copper cylinder on a riser, then quickly to elevate the riser until that droplet of the glue contacts with the SWCNT rope. At the same time, the tip of transducer is adjusted in the three directions to ensure the SWCNT rope is perpendicular to the surface of copper cylinder in stress free condition. Usually, the length of the SWCNT rope between two gluing points is about 0.8~1.2 mm.

Fig. 3.3 Schematic diagram of sample mounting on the MMTD. An on-site picture (a) showing the position on which sample is mounted, indicated by a circle. Three CCD images for the circled position (b), (c), and (d) demonstrating the procedure of sample mounting.

An image of the MMTD system is shown in Fig. 3.4, where the main components and specimens are labelled, including force transducer, DC motor, data acquisition and control unit, lens, CCD camera, and CNT rope. The MMTD system sits on a pneumatic isolation table to minimize the effect of vibration. Since the material of loading tip, borosilicate glass, has a Young's modulus of about 63 GPa, together

with dimensions of the tip, the maximum tensile deformation of the loading tip is calculated to be only $0.003\ \mu\text{m}$, when the maximum load capacity of the force transducer, $0.01\ \text{N}$, is loaded. For all of the creep tests, the displacement of loading tip ranged $10\text{-}60\ \mu\text{m}$, so the deformation of loading tip itself can be neglected. To minimize the deformation of the adhesive, all tests were conducted after at least 6 h of curing. Meanwhile, the loading tip is finely adjusted to ensure the SWCNT rope is always kept in stress free condition. Thus, the displacement of DC motor can be considered as the deformation of sample in tests.

Fig. 3.4 An image of the micromechanical tester device. Main components and specimens, force transducer, displacement motor, data acquisition and control unit, lens, CCD camera and CNT rope, are labeled in the image.

3.1.3 Loading procedure

In creep test, a SWCNT rope sample was loaded in two stages: initial quasi-static ramp, followed by constant load hold. In the ramp stage, samples were stretched at a strain rate of about $1.5 \times 10^{-4}\ \text{s}^{-1}$ to a predetermined load level. Subsequently

in second stage, the force is kept constant until the sample failed or a predetermined loading time, 48 hrs, was reached. All tests were conducted in room temperature of 23°C.

Throughout the creep tests, force-deformation-time data for each sample were recorded. Accordingly, S-N data and creep strain vs. time curves of samples were obtained. As a result, a total of 29 successful creep tests were conducted, including 25 “static fatigue” failure and 4 “survivor” (in which samples survive in the creep tests). Thirteen typical tests were selected for the Burgers model analysis. The morphologies of fracture surfaces of samples in creep were observed by FESEM to reveal the fracture mechanisms of SWCNT ropes. It should be pointed out that each SWCNT rope sample in the study was designated by a uniform format. For instance, for specimen designated “T23-40”, “23” denotes test temperature of sample and “40” denotes sample identity.

3.2 Determination of effective cross-sectional area of sample

As mentioned earlier, the effective cross-sectional area is back-calculated based on a force-deformation curve at initial ramp stage obtained experimentally and an estimated Young’s modulus of SWCNT bundle.

Since large differences exist in Young’s modulus of CNTs obtained from experiments and simulations in previous studies, we calculate the Young’s modulus of SWCNT bundle from the known in-plane Young’s modulus of graphite in the present study. In a bundle, all SWCNTs are well arranged in a two-dimensional hexagonal lattice, shown schematically in Fig. 3.5. The diameter of a SWCNT is denoted by d and the spacing between the adjacent SWCNTs is represented by $2h$. Since each SWCNT can be viewed as a rolled-up graphene sheet, the ratio of the

area of effective graphene sheet in cross section of a bundle, R , is

$$R = \frac{\pi d h}{\sqrt{3}(d/2 + h)^2} \quad (3.1)$$

The Gaussian mean diameter of our SWCNT sample is 1.69 nm [71]. The representative distance between two adjacent graphite layers is 0.34 nm [49], therefore the spacing between the adjacent SWCNTs is considered as 0.34 nm. Based on Eq. (3.1), the ratio, R , is calculated to be 0.51, so the Young's modulus of SWCNT bundle is 51% that of the graphite in plane. The in-plane Young's modulus of graphite is known to be 1060 GPa [96]. The Young's modulus of our SWCNT bundle is estimated to be 540 GPa.

Fig. 3.5 The arrangement of SWCNTs in a hexagonal lattice in a bundle. The diameter of a SWCNT is denoted by d , and the spacing between the adjacent SWCNTs is denoted by $2h$.

In the first stage of loading, the tensile force on a SWCNT bundle, F , is equal to $AE\delta/l$, where A , E , δ , and l are cross-sectional area, Young's modulus, elongation, and initial length, respectively. Based on the linear force-deformation curve obtained experimentally at elastic stage, the slope of the curve is obtained,

which is equal to AE/l . Knowing E and l , A can be easily calculated, which is used to estimate the applied stress on the SWCNT bundles.

3.3 4-element Burgers model

Creep response of all specimens in the study is characterized by a 4-element Burgers model, which is usually used to describe viscoelastic behavior of a number of materials in creep [97]. The model is composed of a spring and dashpot in series with another spring and dashpot in parallel, as shown in Fig. 3.6. It is seen that the Burgers model is composed of three units in series, denoted by three numbers 1, 2 and 3, respectively. Also annotated in the figure are four characteristic parameters, E_1 , E_2 , η_2 , and η_3 , which represent elastic modules and viscosity of the corresponding elements, respectively.

Fig. 3.6 A 4-element Burgers model, including three units [97].

Referring to Fig. 3.6, one can know that total strain in the 4-element model is the sum of strains in units 1, 2, and 3, with same stress in each unit. The total strain, ϵ , and stress, σ , are expressed by the strain and stress for each unit.

$$\varepsilon = \varepsilon_1 + \varepsilon_2 + \varepsilon_3; \quad \sigma = \sigma_1 = \sigma_2 = \sigma_3. \quad (3.2)$$

Here, ε_1 , ε_2 , and ε_3 denote the strain for unit 1, unit 2, and unit 3, respectively; and σ_1 , σ_2 , and σ_3 are the stresses for unit 1, unit 2, and unit 3, respectively. Based on Hookean elasticity and Newtonian viscosity equations, stress and strain relationship for each of three units can be easily obtained. For unit 1, we have

$$\sigma_1 = E_1 \varepsilon_1 \quad (3.3)$$

In this equation, ε_1 is the instantaneous deformation. For unit 2, the stress sustained is the sum of stresses on the spring and the dashpot. The stress on the dashpot is related to the strain rate, $\dot{\varepsilon}_2$. So we have

$$\sigma_2 = E_2 \varepsilon_2 + \eta_2 \dot{\varepsilon}_2 \quad (3.4)$$

For unit 3, which represents Newtonian flow, the relationship between the stress and the strain rate, $\dot{\varepsilon}_3$, is

$$\sigma_3 = \eta_3 \dot{\varepsilon}_3 \quad (3.5)$$

Based on the relationships in Eq. (3.2), three equations (3.3)-(3.5), can be combined into one relating applied stress and the total strain for the Burgers model, as follows.

$$\ddot{\varepsilon} + \frac{E_2}{\eta_2} \dot{\varepsilon} = \frac{1}{E_1} \left[\ddot{\sigma} + \left(\frac{E_1}{\eta_2} + \frac{E_1}{\eta_3} + \frac{E_2}{\eta_3} \right) \dot{\sigma} + \left(\frac{E_1}{\eta_3} \cdot \frac{E_2}{\eta_2} \right) \sigma \right] \quad (3.6)$$

If a constant stress, σ_0 , is instantaneously applied and subsequently held constant (i.e., creep), as shown in Fig. 3.7 (a), the initial condition of Eq. (3.6) is

$$\sigma = \sigma_0, \quad \text{at } t = 0 \quad (3.7)$$

Substituting Eq. (3.7) into Eq. (3.6), Eq. (3.6) is reduced to

$$\ddot{\varepsilon} + \frac{E_2}{\eta_2} \dot{\varepsilon} = \frac{\sigma_0}{\eta_3} \cdot \frac{E_2}{\eta_2} \quad (3.8)$$

The solution of Eq. (3.8) is

$$\varepsilon = \frac{\sigma_0}{E_1} + \frac{\sigma_0}{E_2} \left(1 - e^{-\frac{E_2}{\eta_2} t} \right) + \frac{\sigma_0}{\eta_3} t \quad (3.9)$$

shown in Fig. 3.7 (b). If the creep exceeds the transient time from primary to secondary creep, then

$$\varepsilon = \frac{\sigma_0}{E_1} + \frac{\sigma_0}{E_2} + \frac{\sigma_0}{\eta_3} t \quad (3.10)$$

and the creep strain rate, $\dot{\varepsilon}$, is the steady-state strain rate, i.e., the minimum strain rate, $\dot{\varepsilon}_{ss}$:

$$\dot{\varepsilon} = \dot{\varepsilon}_{ss} = \frac{\sigma_0}{\eta_3} \quad (3.11)$$

It is a very critical parameter, related to the creep mechanism, and often used to offer theoretical guidance for engineering design.

(a)

(b)

Fig. 3.7 Characteristic (a) stress-time and (b) strain-time curves in creep [97].

As we know, the creep mechanism is very complicated, not only because it varies for different materials. Even for the same material, different creep mechanisms might be applied, depending on the inherent microstructure and external environments. To date, no firm nonlinear strain-time relations have been developed, however, an empirical power law for creep has been proposed [93].

$$\varepsilon = \varepsilon_0 + B\sigma^m t + D\sigma^a[1 - \exp(bt)] \quad (3.12)$$

where B , m , D , a and b are empirical constants, and ε_0 is the strain at $t = 0$. Comparing Eq. (3.9) and Eq. (3.12), the reciprocals of characteristic parameters, E_2 , η_2 , and η_3 , could be related to applied stress via a power-law relationship, and $\frac{E_2}{\eta_2}$ is a constant. Suppose that

$$1/E_1 = c_1\sigma^{e_1}, 1/E_2 = c_2\sigma^{e_2}, 1/\eta_2 = c_3\sigma^{e_3}, 1/\eta_3 = c_4\sigma^{e_4} \quad (3.13)$$

where c_1 , c_2 , c_3 and c_4 , and e_1 , e_2 , e_3 and e_4 , are constants. Since $\frac{E_2}{\eta_2}$ is a constant independent of applied stress, e_2 should be equal to e_3 . So we have

$$\begin{cases} \log(1/E_1) = \log c_1 + e_1 \cdot \log \sigma \\ \log(1/E_2) = \log c_2 + e_2 \cdot \log \sigma \\ \log(1/\eta_2) = \log c_3 + e_3 \cdot \log \sigma \\ \log(1/\eta_3) = \log c_4 + e_4 \cdot \log \sigma \end{cases} \quad (3.14)$$

It is known from Eq. (3.14) that e_1 , e_2 , e_3 and e_4 can be determined from log-log plots of $1/E_1$ vs. σ , $1/E_2$ vs. σ , $1/\eta_2$ vs. σ , and $1/\eta_3$ vs. σ for different samples obtained experimentally, respectively. Particularly, emphasis is placed on the constant e_4 , because it is related to the steady-state creep strain rate by $\dot{\varepsilon}_{ss} = c_4\sigma^{e_4+1}$. For some materials which deform with appreciable reduction in area, the stress exponent, $n = e_4 + 1$, is characteristic of creep mechanism [98, 99]. For example, $n = 1$ is associated with the Nabarro-Herring diffusional creep [100], $n = 2$ is expected for grain boundary gliding mechanism [101], $n \sim 4-6$ is expected for a dislocation climb mechanism [102], and $n > 6$ is expected for dislocation movement (e.g. dislocation creep) [103]. In such materials, the strain is extensively homogenous. However, for those materials which deform with negligible reduction in area, such as conventional graphite and SWCNT ropes in the investigation, their plastic strain may be highly localized, and

thus the local strain controlling microscopic mechanism cannot be represented by the observed macroscopic strain behavior. As a result, the interpretation of stress exponent determining deformation mechanism becomes complicated.

The reciprocals of four characteristic parameters for the Burgers model can be obtained by fitting the plots of ε vs. t at different applied stresses obtained experimentally. First, the following two equations can be easily derived from Eqs. (3.9) and (3.11).

$$1/E_1 = \varepsilon_0/\sigma \quad (3.15)$$

$$1/\eta_3 = \dot{\varepsilon}_{ss}/\sigma \quad (3.16)$$

Here, ε_0 is an instantaneous strain at $t = 0$. $1/E_1$ is calculated from Eq. (3.15), determined by the strain at $t = 0$. $1/\eta_3$ is obtained from Eq. (3.16), determined by the steady-state strain rate, $\dot{\varepsilon}_{ss}$, i.e., the slope of the linear portion of the ε vs. t curve at long time. The strain at $t = 0$ expressed by E_1 and the slope of the ε vs. t curve at long time expressed by η_3 are also annotated in Fig. 3.7 (b). $1/E_2$ and $1/\eta_2$ are determined by fitting the ε_2 vs. t curve, where $\varepsilon_2 = \varepsilon - (\varepsilon_1 + \varepsilon_3)$.

The reciprocals of four parameters obtained vary for the samples at different applied stresses. Supposed that the effects of variation among the samples and operative circumstances are negligible, c_1 and e_1 can be obtained by fitting the log-log plot of $1/E_1$ vs. σ based on Eq. (3.14). Similarly, c_2 and e_2 , c_3 and c_4 and e_4 , can also be obtained by fitting the log-log plots of $1/E_1$ vs. σ , $1/\eta_2$ vs. σ , and $1/\eta_3$ vs. σ , respectively. Creep strain of the material is determined at an arbitrary applied stress. Otherwise, the determination of the dependence of the four parameters on applied stress becomes more difficult.

In fact, the effect of the sample variation on creep strain obtained experimentally cannot be often neglected. If the four parameters are influenced by applied stress to a similar or lesser degree than by sample variation, it is assumed for simplicity that the effects are totally attributed to variation among samples, i.e., the four parameters are independent of applied stress. At this time, creep compliance, J , is ε/σ_0 , and it can be expressed in terms of the four parameters.

$$J = \frac{1}{E_1} + \frac{1}{E_2} \left(1 - e^{-\frac{E_2}{\eta_2} t} \right) + \frac{1}{\eta_3} t \quad (3.17)$$

It is only related to four characteristic parameters of the specific sample, independent of applied stresses. For two same samples under different applied stresses, their compliances should be the same even though their strains differ. In order to eliminate the effect of sample variation, the four parameters of the material are presented based on a statistical average of the test results for all samples.

For the i th test of total N tests, the corresponding creep compliance, J_i , can be expressed in terms of four characteristic notations of the i th sample, E_{1i} , E_{2i} , η_{2i} and η_{3i} . Thus, Eq. (3.17) for the i th sample is :

$$J_i = \frac{1}{E_{1i}} + \frac{1}{E_{2i}} \left(1 - e^{-\frac{E_{2i}}{\eta_{2i}} t} \right) + \frac{1}{\eta_{3i}} t \quad (3.18)$$

Using a statistical average of creep compliance, creep compliance of the material can be expressed in terms of characteristic parameters of all of the samples.

$$J = \frac{1}{N} \sum_{i=1}^N J_i(t) = \frac{1}{N} \sum_{i=1}^N \left[\frac{1}{E_{1i}} + \frac{1}{E_{2i}} \left(1 - e^{-\frac{E_{2i}}{\eta_{2i}} t} \right) + \frac{1}{\eta_{3i}} t \right] \quad (3.19)$$

Comparing the items of the right hand side in Eqs (3.17) and (3.19), the sufficient and necessary condition to meet constant equality of all items in the right hand in the two equations is that the following set of equations are required. Thus we get:

$$\begin{cases} \frac{1}{E_1} = \frac{1}{N} \sum_{i=1}^N \frac{1}{E_{1i}} \\ \frac{1}{E_2} = \frac{1}{N} \sum_{i=1}^N \frac{1}{E_{2i}} \\ \frac{1}{\eta_2} = \frac{1}{N} \sum_{i=1}^N \frac{1}{\eta_{2i}} \\ \frac{1}{\eta_3} = \frac{1}{N} \sum_{i=1}^N \frac{1}{\eta_{3i}} \end{cases} \quad (3.20)$$

It is obvious that characteristic parameters of the material can be obtained by calculating harmonic means of characteristic parameters of all samples in tests.

3.4 Results and discussion

3.4.1 Effective cross-sectional areas of specimens

The effective cross-sectional areas of all 29 specimens are calculated, using the method discussed in Section 3.2. The effective cross-sectional areas of 13 selected specimens are summarized in Table 3.1. Thus, at the loading stage of constant force, applied stresses for all samples are calculated and also listed in the table. It can be estimated from the data that the diameter of specimens is in the range of 0.1-1.1 μm . The variation of the effective cross-sectional areas of test samples may result in the diversity of the four characteristic parameters obtained experimentally even if they are at the same applied stress.

Table 3.1 The effective cross-sectional areas of the 13 out of 29 specimens calculated and constant applied stresses on them in creep.

Sample No.	Cross sectional area ($\times 1000 \text{ nm}^2$)	Applied stress, σ (GPa)	Sample No.	Cross sectional area ($\times 1000 \text{ nm}^2$)	Applied stress, σ (GPa)
T23-11	230.6	3.24	T23-41	174.3	7.94
T23-89	335.8	4.52	T23-2	992.5	8.69
T23-40	174.5	4.78	T23-110	161.8	9.41
T23-37	53.4	5.16	T23-30	14.0	9.76
T23-104	586.6	5.81	T23-10	636.8	10.51
T23-56	242.4	6.98	T23-70	187.5	13.89
T23-4	339.4	7.54			

The effective cross-sectional areas are far smaller than measured values of 1-20 μm from CCD images and the ratios in between are calculated for 13 SWCNT ropes, respectively, with the range of 0.03-16.7% and an average value of 2%. This suggests that there exist large amounts of inter-tube gaps or impurities within a SWCNT rope.

3.4.2 S-N data of SWCNT bundle

Stress-life (S-N) test data are usually displayed on S-logN plot and assumes a simple linear relation below.

$$\sigma_{\alpha}/\sigma_{ult} = 1 - m \log N \quad (3.21)$$

where σ_{α} and σ_{ult} are applied and ultimate stress, respectively, $\sigma_{\alpha}/\sigma_{ult}$ is

normalized stress, N is the number of cycles to failure, similar to time-to-failure for static fatigue, and m the slope of the normalized S-N curve.

S-N data obtained experimentally from 29 tests of SWCNT rope specimens at room temperature, as well as a typical straight line obtained by fitting 25 “static fatigue” data based on Eq. (3.21), are plotted in Fig. 3.8. It is found that the fitted straight line is in good agreement with experimental data, with a middle coefficient of determination (a measure of how well the regression line represents the experimental data), i.e., the values of R-square, 0.534, showing static fatigue of SWCNT bundle has a typical linear normalized S-N curve. It is calculated from the fitted straight line that ultimate stress, σ_{ult} , and the slope of the normalized S-N curve, m , are 17.77 GPa and 0.142. More details have been reported [41].

Fig. 3.8 Stress-life (S-N) diagram of SWCNT bundle at room temperature.

3.4.3 Creep strain versus time curves of SWCNT bundle

Creep strain versus time curves of 13 selected SWCNT rope samples obtained experimentally, as well as corresponding fitted curves for the 13 tests by 4-element Burgers model, are plotted in Fig. 3.9. In the figure, the labels are sorted by the magnitude of applied stress, ranged from 3.24 GPa for sample T23-11 to 13.89 GPa for sample T23-70. In order to clearly view the data of samples with short rupture time, the full time scale shown in Fig. 3.9 is not set to be the longest test time for all samples but 10^4 s, which exceeds the transient from primary to steady-state creep for all samples.

Fig. 3.9 Experimental and fitted creep strain vs. time curves of 13 SWCNT bundles at 23°C by the Burgers model within the time scale of 10^4 s.

It is found from Fig. 3.9 that when applied stress is higher than that of sample T23-41, i.e., at 7.94 GPa, creep rupture occurs for most samples at less than 5000 s,

except that sample T23-2, which survives at 10^4 s. The creep curve of sample T23-2 shows strong fluctuations after 5000 s, probably because the existence of relatively more defects, originated from its maximum cross-sectional area in all samples, results in fractures of more SWCNT bundles or subbundles within the SWCNT rope specimen. At low stresses less than 7.94 GPa, the steady-state strain rate regularly varies in the way that it increases first and then decreases with increasing applied stress and reaches the maximum at the stress of sample T23-37, 5.16 GPa. This implies that the applied stress higher than 5.16 GPa would lead to strengthening of the structure of sample. Various hardening mechanisms [104], including continued graphitization, change of creep mechanism, crack healing, and changes in dislocation structure, could be used to explain the tensile creep behavior.

It is seen from the Fig. 3.9 that the fitted curves fit well with experimental data, except that some discrepancies occur in primary creeps of the samples, T23-11 and T23-104. This implies that the Burgers model can be used to characterize the tensile creep behavior of SWCNT bundle at room temperature, for the main concern in common engineering design is the steady-state creep. Using the fitting method described above, the four parameters for each SWCNT rope sample are obtained. The four parameters for all of 13 selected samples, as well as their harmonic mean values, are summarized in Appendix I. It is found from these data that large differences exist in each characteristic parameter among different samples, however, their reciprocals are relatively close, which is directly related to creep strain behaviour of sample.

Log-log plots of the four reciprocal parameters vs. applied stress and their linear fits are shown in Fig. 3.10. The values of the slope and R-square of the fitting line for each parameter are annotated on a corresponding plot. Four constants in

Eq. (3.13), e_1 , e_2 , e_3 , and e_4 , are approximately determined by the slopes of the fitting lines to be -0.23, -1.06, 0.89, and 0.75, respectively. However, the fits have low values of R-square and they are 0.087, 0.318, 0.074, and 0.028, respectively, so the dependence of the four parameters on applied stress cannot be effectively modeled by these straight lines and become more difficult to be determined. This is due to the strong impact of sample variation on tensile creep behavior.

Fig. 3.10 Log-log plots of (a) $1/E_1$ vs. σ , (b) $1/E_2$ vs. σ , (c) $1/\eta_2$ vs. σ , and (d) $1/\eta_3$ vs. σ and their linear fits. The slopes of the fitted straight lines and R-square values of the fits are annotated.

The rough trends of the dependence of the four parameters on applied stress

indicated the four fitted lines in Fig. 3.10 are weak, with the values of the slopes ranged from -1.06 to 0.75 (close to 1). Together with the restriction relationship of $e_2 = e_3$ mentioned earlier, it is assumed that four constants, e_1 , e_2 , e_3 , and e_4 , are all zero for simplicity. This implies that E_1 , E_2 , η_2 , and η_3 , are stress-independent constants and the variations in their experimental values from different tests are attributed to the effect of variation in sample, as well as “noise” in the data. Based on Eq.(3.20), these experimental values of $1/E_1$, $1/E_2$, $1/\eta_2$, and $1/\eta_3$ for all samples are statistically averaged to be as those for the SWCNT bundle material. The values of E_1 , E_2 , η_2 and η_3 are obtained to be 462 GPa, 858 GPa, 8.8×10^5 GPa·s and 1.22×10^7 GPa·s, respectively.

With the calculated values of the four parameters, the creep compliance of the SWCNT bundle material at room temperature is plotted against time, as shown in Fig. 3.11. It is noted that the creep compliance curve is characteristic of an average creep compliance behavior of SWCNT bundles at room temperature under the applied stress in the range of 3.24-13.89 GPa. It does not account for possible effect of applied stress on the creep compliance, so some discrepancies might appear when it is applied to characterizing the creep behavior of SWCNT bundles under a specific value of applied stress. The steady-state strain rate is in proportion to applied stress and the ratio is about 8.2×10^{-8} GPa⁻¹·s⁻¹. The creep compliance curves of 13 selected samples obtained experimentally are shown in the Fig. 3.11 for comparison. It is found from Fig. 3.11 that the calculated curve is located in the middle of a cluster of the curves obtained experimentally, so that it can be considered as an effective representative characterizing overall creep compliance behaviors. It is also found that significant differences exist in creep compliances of different samples, which are attributed to sample variation and possible dependence of the four characteristic parameters on applied stress. The latter cause is discussed as follows.

Possible influence of applied stress on E_1 , E_2 , and η_2 are not discussed here, since they are not associated with the steady-state strain rate in creep, $\dot{\epsilon}_{ss}$, a very important parameter in engineering design. Emphasis is placed on the dependence of η_3 on applied stress. Referring to Fig. 3.10 (d), it is clear that the data cannot be fitted by a single line, while they may be modeled with several lines, as shown in Fig. 3.12.

Fig. 3.11 Creep compliance vs. time curves for the SWCNT bundles at room temperature of 23°C.

Fig. 3.12 A quadrilinear fit of $\log(1/\eta_3)$ vs. $\log\sigma$. The slopes of four lines and corresponding R-square values are annotated.

It is found from Fig. 3.12 that the quadrilinear fit well coincides with experimental data. For the first line in which applied stress is in the range of 3.24-5.16 GPa, the slope is 6.98 and R-square is 0.836, showing very high satisfaction of fit. Related stress exponent, n , is obtained to be 7.98, in the range of 5.5-8 values reported for various coke-pitch graphites under tensile stresses [98]. The high n value does possibly but not necessarily imply a dislocation creep mechanism, because the local n controlling microscopic mechanism might be far lower than the observed value. In the second stage of the multi-line, the slope is -8.7, i.e., the n value is -7.7, implying possible continued graphitization, crack healing, changes in dislocation structure, and change of creep mechanism. When applied stress increases again, $\dot{\epsilon}_{ss}$ sharply increases, probably due to more dislocation creep by numerous defects. All of this show that the observed macroscopic $\dot{\epsilon}_{ss}$ is very complicated, which is difficult to determine the microscopic $\dot{\epsilon}_{ss}$ -controlling creep mechanism. Defects in SWCNT rope samples play a dominate role in controlling tensile creep behavior, for they are related to the local

$\dot{\epsilon}_{ss}$ controlling creep mechanism.

3.4.4 Fracture morphology analysis

The fracture morphology of the SWCNT rope that failed during creep test is examined using FESEM, as shown in Fig. 3.13 and Fig. 3.14. Fracture occurs at a subbundle level, with splitting and numerous brittle fractures of subbundles.

It is seen from Fig. 3.13 that SWCNT bundles fracture stepwise at different locations, probably due to the difference in locations of defects distributed along the SWCNTs. The defects give rise to strain localization and stress concentration, leading to fracture of some bundles. The fracture of some bundles causes decreasing bundles to sustain the constant tensile load during static fatigue tests when weaker bundles failed. This does powerfully support the stepped fracture of SWCNT bundle described in previous report that the remaining SWCNTs in a SWCNT rope undergo increasing stress during static fatigue when a subbundle or bundle fractures [41]. More importantly, it coincides with the defect-controlling tensile creep behavior of SWCNT rope at room temperature obtained by Burgers model analysis.

However in Fig. 3.14, a number of rather flat fracture surfaces are seen in the subbundles oriented more or less parallel to the loading direction and no individual SWCNT is split out. Moreover, the fracture surfaces are at approximately the same location in a bundle. This suggests not only brittle fracture but also a local load shearing mechanism between bundles within the SWCNT rope. A fracture of a subbundle or bundle may cause a local stress concentration. The additional stress was taken up by those SWCNTs surrounding the failed nanotubes, thus to give rise to faster fracture of the remaining nanotubes in the vicinity of the particular site.

Fig. 3.13 A FESEM image of fracture surface of a SWCNT rope with the splitting and cutting-off of SWCNTs, showing that SWCNT subbundles fracture subsequently rather than simultaneously.

Fig. 3.14 A FESEM image of fracture surface of a SWCNT rope with the splitting and cutting-off of SWCNTs, showing that no individual SWCNT is split out within the subbundles, with flat brittle-like fracture surfaces.

3.5 Conclusions

We have performed tensile tests of SWCNT rope at room temperature under constant applied stress. S-N data and creep strain vs. time curves have been obtained experimentally. The S-N data show a typical linear normalized S-N curve for static fatigue of SWCNT bundle. The fatigue strengths of SWCNT bundle are doubled within 10^4 s and similar at longer times. The fatigue limits of SWCNT bundles seem to exist at 4-5 GPa within the time scale of 48 hours. The creep strain vs. time curves can be well fitted by a 4-element Burgers model. As a result, four characteristic parameters for each sample have been obtained. However, the four parameters measured experimentally are influenced by sample variation and different applied stress. And the degree of influence by sample variation is similar or higher than that by applied stress. Creep mechanism is difficult to be simply determined by stress exponent, and it is controlled by defects in samples. Based on a hypothesis that the four parameters are independent of applied stress, the harmonic means of characteristic parameters of all samples in tests are calculated to wash out the effect of sample variation and “noise” in the data. An average creep compliance behavior of SWCNT bundles at the applied stress in the range of 3.24-13.89 GPa is obtained, presenting the applied stress-independent creep compliance behavior on a whole. The steady-state strain rate is in proportion to applied stress and the ratio is about $8.2 \times 10^{-8} \text{ GPa}^{-1} \cdot \text{s}^{-1}$. Effect of temperature on creep behavior will be described in detail in Chapter 4.

Moreover, we have also observed the morphologies of fracture surfaces of SWCNT bundles through FESEM examination. The results show that fractures occur at a subbundle level, with splitting and numerous brittle fractures of SWCNT subbundles. SWCNT bundles fracture stepwise at different locations, probably due to the difference in locations of defects distributed along the SWCNTs. This

coincides with the defect-controlling creep behavior of SWCNT rope at room temperature obtained by Burgers model analysis. However, how do defects affect the fracture of SWCNT bundle is still not clear, which will be investigated in Chapter 5.

CHAPTER 4

EFFECT OF TEMPERATURE ON TIME-DEPENDENT BEHAVIOR OF SWCNT BUNDLE UNDER STATIC TENSION

In Chapter 3, time-dependent behavior of aligned SWCNT bundles at room temperature was investigated experimentally. Since creep is a thermally activated molecular motion process in nature, creep strain rate varies with temperature. We consider static fatigue lives and creep strain behaviors of SWCNT bundles at slightly elevated temperatures, 38° and 54°C. Combined with the result obtained in Chapter 3, the effect of temperature on static fatigue life and creep strain behaviors of SWCNT bundles is demonstrated. Stress-life (S-N) data at three different temperatures are obtained and compared, indicating that elevated temperature may cause strengthening or weakening of the structure of SWCNT bundle dependent of the magnitude of temperature. Creep compliance curves of SWCNT bundles against logarithmic time at three different temperatures are plotted and compared, taking on a characteristic of the similarity in shape. By horizontal shift along the log (time) axis, a single master curve at 23°C is generated, to check the validity of time-temperature superposition (TTSP) principle. The master curve can be applied to predict creep behavior of SWCNT bundles at an arbitrary temperature or long-term creep behavior at lower temperatures to save testing time.

4.1 Introduction

Creep is a thermally activated molecular motion process and creep strain rate increases as temperature rises. CNTs, with their unique mechanical properties and excellent thermal stability, could be building blocks for various structural materials subjected to heat for a long time. Hence, it is useful and necessary to perform a comprehensive study on creep behaviors of the CNTs at different temperatures for engineering applications.

In the past decade, thermal and mechanical properties of CNTs have been extensively investigated and influences of environmental temperature on their mechanical properties have been also reported [11, 34-40, 105-110]. However, reports on creep behaviors of CNTs and their composites are very limited [47, 93-95, 111-113]. Among them, very few is concerning creep behaviors of CNTs themselves [93]. Most studies are concerned with creep behaviors of various CNT composites, which have been reviewed in Chapter 2 [47, 94, 95, 111-113]. Creep strain rate of CNTs polymer composites reduces with decreasing temperature and increased content of CNTs [95, 111]. TTSP has been applied to creep compliance of MWCNTs/polypropylene composites at different temperatures to construct a master curve of the creep compliance at a reference temperature based on the William-Landel-Ferry (WLF) equation, to predict the long-term creep behavior[47, 95]. However, the effect of temperature on creep behavior of CNTs themselves has been receiving less attention. Our attempt is to conduct a preliminary study on creep behaviors of aligned CNT bundles at different temperatures.

In practice, regular creep tests are time-consuming and expensive. To overcome these difficulties, a technique known as TTSP principle is usually used to construct

a master curve at a reference temperature to predict long-term creep behavior [97]. The TTSP method will be described in detail in Section 4.2.

In this chapter, we explore the influence of temperature on CNT's creep behaviors. Since the sensor within force transducer cannot work well at temperatures above 60°C, the maximum test temperature was limited to be below 60°C on the condition that no effective insulation measures are taken to protect the sensor. Two arbitrary temperatures between room temperature and 60°C, 38°C and 54°C, are selected. At the two selected temperatures, tensile creep tests are performed for aligned SWCNT bundles and creep strain-time curves are obtained accordingly. Similarly to creep strain and creep compliance curves of samples at 23°C obtained in Chapter 3, corresponding quantities at 38°C and 54°C are also obtained. Master curve of creep compliance is generated using TTSP method, to predict creep behavior at an arbitrary temperature or long-term creep behavior at lower temperatures.

4.2 TTSP method

TTSP was first identified by Leaderman in 1943, through experimental observations on creep behavior of a range of materials at different temperatures [114]. It was found that creep compliance curve at any given temperature was independent of applied stress for various materials and that creep compliance plots in terms of $\log(\text{time})$ are of the same shape for different temperatures, and that change of temperature had an influence of extending or contracting the time scale. Subsequently, based on Leaderman's observations, individual creep compliance curves at different temperatures were first shifted along the $\log(\text{time})$ axis to generate a single curve at a reference temperature, known as a master curve [115].

If this method is valid, known as TTSP, the master curve generated represents the real long-term creep behavior at the reference temperature.

To date, there are no fixed rules for generating a master curve yet, although TTSP has been widely used for many decades. In practice, we treat a necessary condition for a master curve that the curve would be smooth as its sufficient condition to allow reliance on the TTSP method. Usually for some materials under some specific test conditions, a smooth master curve can be generated by shifting horizontally along the log (time) axis. However, for others materials and/or under variable test conditions, where thermal expansion and contraction cannot be ignored, it is too difficult to superpose completely if only a horizontal shift is allowed. Then, a vertical shift is needed to be added, which does account for the effects of these variable test conditions. Usually the changes of test conditions involve those of material density, environmental humidity, and so on.

In this study, temperature changes are not large with a maximum range of 31°C. Thermal contraction of all SWCNT rope samples can be estimated to be less than 0.05% [116] according to axial coefficient of thermal expansion of SWCNT, $\alpha > -1.6 \times 10^{-6} \text{ K}^{-1}$ [115, 117], which is negligible compared to creep strain. Moreover, the material density and environment humidity only change slightly for all temperature levels. Therefore, no vertical shift factor is needed, and only a horizontal shift is expected to be sufficient. However, since SWCNT bundles are in crystalline phase, the most common one of various empirical expressions for horizontal shift factor, the WLF equation [41], cannot be used here, because it is limited to the condition that test temperature is above glass transition temperatures of materials.

Considering that creep is a thermally activated process and follows Arrhenius equation, creep relaxation time, t , can be associated with temperature, T :

$$t = B \exp\left(\frac{-Q}{RT}\right) \quad (4.1)$$

Where B is a reciprocal factor of frequency, Q is the activation energy, and R is the universal gas constant with the value of 8.314 J/mol·K. In general, B and Q are temperature independent, except for those covering a wide temperature range, in which B is usually allowed to be proportional to T for more precise analysis. In this study with a maximum temperature range of 31°C, B can be treated as temperature independent.

Therefore, the ratio α_t of creep relaxation time at an arbitrary temperature, T , to its value at a reference temperature, T_r , can be given by:

$$\alpha_t = \exp\left[\frac{-Q}{R}\left(\frac{1}{T} - \frac{1}{T_r}\right)\right] \quad (4.2)$$

The reference temperature, T_r , is set as room temperature (296K), since the long-time applications of the material usually happen at room temperature. Based on Eq. (4.2), the so-called horizontal shift factor in generating master curve, $\log(\alpha_t)$, is:

$$\log(\alpha_t) = \frac{-Q}{2.303R}\left(\frac{1}{T} - \frac{1}{T_r}\right) \quad (4.3)$$

It should be pointed out that if the TTSP theory is valid, it is required that creep mechanisms are the same at all the temperatures. This means the same activation energy in the creeps at different temperatures, which is in turns used for checking the validity of the TTSP theory.

4.3 Experiments

4.3.1 Specimens and experimental set-up

The specimens used are aligned SWCNT bundles with the length of about 1.5-3 mm and 1-20 μm in width or diameter, similar to those used in Chapter 3.

All creep tests are carried out in the Micro-mechanical testing device (MMTD) described in Chapter 3. However, since different temperatures are involved, a heating system made in house is added, the whole experimental set-up is shown schematically in Fig. 4.1. Test sample, as well as a copper cylinder connecting with the bottom of sample, is placed into the heater block. Inside the heater block there are three thermocouples, of which two are hanged from the upper surface of the heater block and connected with a thermometer to measure the surrounding temperatures of test sample and the third one is connected with the control panel to adjust and control internal temperature of the heater block. An image of the heating system is shown in Fig. 4.2, where three main components, (1) a rectangular heater block, (2) three thermocouples, and (3) a control panel, are annotated.

Fig. 4.1 A schematic MMTD with a heating system: (A) loading tip, (B) force transducer, (C) displacement motor, (D) data acquisition and control unit, (E) lens/CCD camera, (F) copper cylinder, (G) riser, (H) SWCNT rope, (I) glue, (J) thermocouples, (K) heater block, (L) control panel of heater, (M) thermometer.

Fig. 4.2 A heating system attached to the MMTD, including (1) heater block, (2) three thermocouples, and (3) control panel. A coordinate system, xyz , is annotated and x direction points at the front view.

The dimension of the rectangular heater block is $45 \times 43 \times 15$ mm. It is made of mica in the whole shell plate with an inner brass center for insulation, which can be viewed from an image of bottom side of heater block in Fig. 4.3. At the bottom of the block there is a hole reserved for the brass center holding copper cylinder to be mounted and dismounted. Some grooves are reserved on the shells in the front and two side of the heater block for special functions. A hole on top insulation is

reserved for upper loading tip to be inserted or withdrawn. Two small U-shaped grooves on the left and right side are designed for side view visualization, which is used for mounting sample to ensure the verticality of sample from side view and capturing test process and for taking high magnification images for post test analysis. The front open groove is for sighting line from front view when mounting sample. Inside the heater block there are seven cartridge heaters, each encapsulated inside the stainless steel heating block for better thermal transmission.

Fig. 4.3 A view of bottom side of the heater block, with the brass center holding copper cylinder pulled out.

Referring to Fig. 4.2, two thermocouples are placed on two sides of the sample after it is mounted for real-time temperature measurement. Seven cartridge heaters and another thermocouple are connected with a control panel, which can

regulate the heater and control temperature. The temperature shown on control panel is the heater temperature, always higher than sample temperature measured by the other two thermocouples. However, by pre-setting the temperature on control panel, sample temperature can be determined when heating is stabilized. The heater block is placed below the tip of force transducer and sits on a pneumatic isolation table together with micromechanical tester to minimize the effect of vibration.

To mount a sample on the micromechanical tester with heating system, the following steps are followed: (i) referring to Fig. 4.3, a clean 12 mm-diameter, 5 mm-high copper cylinder is placed into the mica brass centre, and then the whole brass centre containing copper cylinder is inserted into the heater block from the bottom, and finally the heater block is fixed on a riser; (ii) the tip of force transducer is adjusted in x , y and z directions as shown in Fig. 4.2 and then the riser is elevated to ensure the tip is located in the middle of the hole on top insulation of the heater block, which can be checked from the front by eye and side view visualization (see Fig. 4.4); (iii) the riser is lowered to allow withdrawal of the loading tip from the front hole of heater block, and to keep enough distance in between to ease subsequent application of adhesive onto the surface of copper cylinder inside the heater block; (iv) a drop of adhesive is added onto the tip below the force transducer; (v) a selected SWCNT rope is adhered which has been placed on the tweezers to the tip of force transducer; (vi) another drop of adhesive is added on the surface of the copper cylinder inside the heater block, then the riser is quickly elevated until that droplet of adhesive contacts with the SWCNT bundle, at the same time, the tip of transducer in x , y and z directions is adjusted to ensure the SWCNT bundle is perpendicular to the surface of copper cylinder in stress free condition.

A SWCNT rope mounted on the tester is shown in Fig. 4.5. Usually, the lengths of the SWCNT bundle between two gluing points are about 0.8-1.2 mm. The deformations of loading tip and copper holder were neglected, which was similarly described in Chapter 3. All tests were conducted after at least 6 h of the glue curing to minimize the deformation of the adhesive.

Fig. 4.4 A side view of an appropriate location of loading tip, with contour profile of side groove presented.

Fig. 4.5 A SWCNT rope mounted on the MMTD with a heating system.

4.3.2 Testing procedure

Two sets of creep tests were performed at 38° and 54°C, respectively. Load applications include two stages: initial quasi-static ramp, followed by a constant load. In the ramp stage, samples were stretched at a strain rate of about $1.5 \times 10^{-4} \text{ s}^{-1}$ by moving loading tip to a predetermined load level, when the temperature remain at 23°C. In the constant-load stage, loading mode was changed into load control from previous displacement control. And the heater temperature was regulated to 55° and 80°C, respectively, and it was kept constant. After heating was stabilized, the sample temperatures measured were about 38° and 54°C, respectively. Temperature ramp from 23° to 38°C (or 54°C) lasted only 1-2 minutes. A total of 33 successful tests were conducted, including 13 tests at 38°C and 20 tests at 54°C. Similar to the tests at 23°C, they both consisted of “static fatigue” and “survivor”. 14 typical tests, one half at 38°C and the other half at 54°C, were selected for the Burgers model analysis. As mentioned in Chapter 3,

samples are designated by a uniform format. For instance, specimen designated “T38-56”, “38” denotes test temperature of sample and “56” denotes sample identity.

4.4 Fitting creep curves

Creep strain vs. time curves of 14 selected specimens were obtained at constant stresses. In these creep tests, force-displacement-time data were directly recorded. Using the force-deformation data at elastic stage at 23°C, the effective cross-sectional areas of the specimens can be estimated based on the Young’s modulus of SWCNT bundle of 540 GPa calculated in Chapter 3. Knowing the cross-sectional area of a specimen and the constant applied force, the applied stress for the specimen can be calculated.

Referring to the method by which experimental data at 23°C are processed and analyzed in Chapter 3, the same method is employed to analyze creep responses (strain-time curves) of 14 selected specimens at the two higher temperatures. Based the Burgers model, four characteristic viscoelastic parameters for each curve were obtained by some curve fitting. By calculating harmonic mean values of characteristic parameters obtained from all selected creep tests at the same temperature level, average creep compliance curves of the CNT bundle at 38° and 54°C are obtained, with creep duration of up to 15 hours to ensure to enter the steady state stage of creep. The effect of sample variation on creep behavior of the material was eliminated.

4.5 Results and discussion

4.5.1 Effective cross sectional areas of specimens

The effective cross-sectional areas of samples have also been estimated at higher temperatures similarly described in Section 3.4.1, based on the Young's modulus of SWCNT bundle and force-displacement data at initial stages of tests when temperature is still 23°C. Assuming that the influence of temperature on effective cross-sectional areas of specimens is neglected, the calculated effective cross-sectional areas of 14 specimens at 38° or 54°C are summarized in Table 3.1. The diameter of the specimens calculated is in the range of 0.1-0.9 μm , which is far smaller than measured value of 1-20 μm from CCD images. This suggests that there are large amounts of inter-tube gaps or impurities within a SWCNT rope. The variation of the effective cross-sectional areas of test samples may result in the diversity of the four characteristic parameters obtained experimentally even if they are tested at the same applied stress.

Table 4.1 The calculated effective cross-sectional areas of 14 selected specimens and constant applied stresses in creep, of which one half are tested at 38°C and the other half are done at 54°C.

Sample No.	Cross sectional area ($\times 1000 \text{ nm}^2$)	Applied stress, σ (GPa)	Sample No.	Cross sectional area ($\times 1000 \text{ nm}^2$)	Applied stress, σ (GPa)
T38-54	225.4	5.25	T54-91	592.0	7.65
T38-70	233.6	6.97	T54-96	79.3	8.24
T38-56	235.1	7.49	T54-93	604.2	8.46
T38-52	72.1	11.64	T54-92	784.4	9.32
T38-51	40.5	12.22	T54-95	84.2	10.78
T38-55	120.7	15.10	T54-76	40.2	11.12
T38-74	39.8	19.12	T54-84	9.0	12.74

4.5.2 S-N data

Two sets of S-N data were obtained experimentally from 13 tests of SWCNT rope specimens at 38°C and 20 tests at 54°C, respectively. They are plotted in Fig. 4.6, together with S-N data obtained at 23°C in Chapter 3. Comparing the two sets of data points at 23° and 38°C, it is seen that fatigue strengths of SWCNT bundles at 38°C are obviously higher than those at 23°C, suggesting that elevated temperature leads to strengthening of the structure of samples. This could be attributed to possible hardening mechanisms, including continued graphitization, crack healing, changes in dislocation structure, and change of creep mechanism [104]. When temperature is up to 54°C, the fatigue strengths of sample decrease compared with the corresponding values at 38°C, especially at higher applied stress. It implies possible occurrence of damage of the structure of sample at this temperature.

Fig. 4.6 S-N diagram of SWCNT bundle at three temperatures, 23°, 38°, and 54°C. “Static fatigue” data are fitted by a straight line. “Survivor” data are indicated by arrows.

Based on Eq. (3.21), “static fatigue” data at each temperature level are fitted by a straight line, also shown in Fig. 4.6. It is found that two fitted straight lines at 38° and 54°C, with R-square values of 0.227 and 0.014, respectively, have less satisfaction than that at 23°C (R-square=0.534), which could be due to more obvious influence of sample variation on tensile creep behavior and stronger “noise” in the data at higher temperatures. The fatigue strength of SWCNT bundle at 38°C is about 1.5 times that at 23°C within 10^4 s, and the fatigue limit is estimated to 9 GPa or so within the time scale of investigation, similar to the corresponding value at 54°C. However, the fatigue strength at 54°C is lower within 3400 s and subsequently higher than the corresponding value at 23°C.

4.5.3 Creep behaviors at different temperatures

Creep strain versus time curves of 7 selected SWCNT rope samples obtained experimentally at 38°C, as well as the fitted curves by the 4-element Burgers model, are plotted in Fig. 4.7. In the figure, the labels are sorted by the magnitude of applied stress, ranged from 5.25 GPa for sample T38-54 to 19.12 GPa for sample T38-74. In order to clearly view the data of samples with short rupture time, the full time scale shown in Fig. 4.7 is not set to be the longest test time for all samples but 10^4 s, which exceeds the transient from primary to steady-state creep for all samples.

Fig. 4.7 Experimental and fitted creep strain vs. time curves of 7 selected SWCNT bundles at 38°C by the Burgers model within the time scale of 10^4 s.

It is seen from Fig. 4.7 that three creep tests lasted more than 8,000 s and the other four tests lasted less than 3,000 s. The applied stresses corresponding to the tests with longer time-to-failure are not lower, which is affected by sample variation.

It is found that to some extent, a larger cross-sectional area of sample leads to shorter time-to-failure and smaller creep strain, which is probably attributed to more defects within the thicker samples, implying that defects play a crucial role in creep behavior of SWCNT bundles. The fitted curves are in very good agreement with experimental data, indicating that the model can be used to characterize the creep behavior of SWCNT bundle at 38°C. At the same time, four parameters, E_1 , E_2 , η_2 and η_3 , for the SWCNT bundle are obtained. All characteristic parameters for the 7 SWCNT bundles, as well as their harmonic mean values, are summarized in Appendix II. It is found from these data that large differences exist in each characteristic parameter among different samples, however, their reciprocals are relatively closed, which is directly related to creep strain behaviour of sample.

Based on the analysis of the dependence of the four parameters at 23°C on applied stress and sample variation in Chapter 3, for simplicity, E_1 , E_2 , η_2 , and η_3 , are supposed to be stress-independent constants and the variations in their experimental values from different tests are totally attributed to the effect of sample variation. In order to eliminate the effect of sample variation, E_1 , E_2 , η_2 , and η_3 for the SWCNT bundle material are obtained by calculating harmonic means of corresponding quantities for all selected samples obtained experimentally based on Eq.(3.14). The four parameters, E_1 , E_2 , η_2 and η_3 , for the SWCNT bundle at 38°C are: 387 GPa, 207 GPa, 1.0×10^5 GPa·s and 3.67×10^6 GPa·s, respectively, as listed in Table 4.2 together with corresponding quantities at 23°C obtained in Chapter 3. It is obvious that the values of E_1 , E_2 , η_2 and η_3 at 38°C are lower than corresponding quantities at 23°C, suggesting that creep resistance behavior of CNT bundle is deteriorated with increasing temperature.

With the four characteristic parameters, E_1 , E_2 , η_2 and η_3 for the SWCNT

bundle, the creep compliance of SWCNT bundle at 38°C, with a duration of up to 15 hours, is plotted against time in Fig. 4.8. It is noted that the creep compliance curve is characteristic of an average creep compliance behavior of SWCNT bundles at 38°C under the applied stress in the range of 5.25-19.12 GPa. It does not account for possible effect of applied stress on the creep compliance, so some discrepancies might appear when it is applied to characterizing the creep behavior of SWCNT bundles under a specific value of applied stress. The steady-state strain rate is in proportion to applied stress and the ratio is about $2.7 \times 10^{-7} \text{ GPa}^{-1} \cdot \text{s}^{-1}$, far higher than corresponding value of $8.2 \times 10^{-8} \text{ GPa}^{-1} \cdot \text{s}^{-1}$ at 23°C, showing an increase of creep strain rate at the same applied stress with increasing temperature. The creep compliance curves of 7 selected samples obtained experimentally are shown in Fig 4.8. for comparison. It is found from Fig. 4.8 that the calculated curve is located in the middle of a cluster of the curves obtained experimentally, showing an effective representative characterizing overall creep compliance behaviors.

Fig. 4.8 Creep compliance vs. time curves for SWCNT bundles at 38°C.

Similarly, creep strain versus time curves of 7 selected SWCNT rope samples obtained experimentally at 54°C, as well as the fitted curves by the 4-element Burgers model, are plotted in Fig. 4.9. It is seen from Table 3.1 that effective cross-sectional areas of three samples, T54-91, T54-93, and T54-92, are close, far larger than those of the remaining 4 samples at 54°C. It is found from Fig. 4.9 that the curves for the thicker samples are just located below the other curves, which confirms again that thicker samples of SWCNT rope give rise to small creep strain. The sample T54-92 is the maximum effective cross-sectional area and its time-to-failure is the shortest, which confirms again that thicker samples have shorter life. All of this implies that sample variation strongly affects tensile creep behavior of SWCNT rope samples, suggesting that defects in SWCNT rope samples play a dominant role in controlling tensile creep behavior.

Fig. 4.9 Experimental and fitted creep strain vs. time curves of 7 selected SWCNT bundles at 54°C by the Burgers model within the time scale of 10^4 s.

Good agreement of the fitted curves with experimental data suggests that the 4-element model is suitable for characterizing creep behavior of SWCNT bundles at different stresses and at specific temperatures in the study. At the same time, the four parameters, E_1 , E_2 , η_2 and η_3 for SWCNT bundle at 54°C are obtained. Four characteristic parameters for each of 7 samples at 54°C and their harmonic mean values are summarized in Appendix III. Based on Eq.(3.14), the harmonic mean values of E_1 , E_2 , η_2 and η_3 are approximately considered to be four characteristic parameters for the SWCNT bundle material at 54°C under the applied stress in the range of 7.65-12.74 GPa. They are calculated to be 342 GPa, 160 GPa, 6×10^4 GPa·s and 2.45×10^6 GPa·s, respectively, as are also listed in Table 4.2 and the lowest among those obtained in the 3 different temperatures, to confirm again that creep resistance of CNT bundle decreases with increasing temperature.

Table 4.2 The harmonic mean values of four characteristic parameters for SWCNT bundles modelled by a 4-element Burgers model at three different temperatures.

Temperature (°C)	$E_1(10^2\text{GPa})$	$E_2(10^2\text{GPa})$	$\eta_2 (10^6\text{GPa}\cdot\text{s})$	$\eta_3 (10^6\text{GPa}\cdot\text{s})$
23	4.62	8.58	0.88	12.17
38	3.87	2.07	0.10	3.67
54	3.42	1.60	0.06	2.45

With the harmonic mean values of E_1 , E_2 , η_2 and η_3 for the SWCNT bundle at 54°C, the same 15-hour creep compliance of SWCNT bundle at the temperature is plotted against time, as shown in Fig. 4.10. The creep compliance curve is characteristic of an average creep compliance behavior of SWCNT bundles at 54°C under the applied stress in the range of 7.65-12.74 GPa, where the possible effect of applied stress on the creep compliance is not taken into account. At the steady stage, the derivative of creep compliance of SWCNT bundle with respect to

time, is about $4.1 \times 10^{-7} \text{ GPa}^{-1} \cdot \text{s}^{-1}$, higher than corresponding values of $8.2 \times 10^{-8} \text{ GPa}^{-1} \cdot \text{s}^{-1}$ at 23°C and $2.7 \times 10^{-7} \text{ GPa}^{-1} \cdot \text{s}^{-1}$ at 38°C , showing higher temperature will cause a faster increase of creep strain rate at the same applied stress.

The creep compliance curves of 7 selected samples obtained experimentally at 54°C are shown in Fig. 4.10 for comparison. It is found that the calculated compliance curve is located in the middle of a cluster of the curves obtained experimentally within 4000 s, showing that a representative of overall creep compliance behaviors.

Fig. 4.10 Creep compliance vs. time curve for SWCNT bundles at 54°C .

4.5.4 TTSP for creep compliance

Comparing the three sets of harmonic mean values of characteristic parameters at 23° , 38° and 54°C listed in Table 4.2, it is found that the elastic and viscous parameters decrease with increasing temperature, showing weakening of creep

resistance with increasing temperature. With the harmonic mean values, creep compliances vs. logarithmic time curves at three different temperatures are plotted based on the 4-element Burgers model, as shown in Fig. 4.11. For each creep compliance curve, the creep duration is up to 15 h to ensure that the steady creep state is reached. It is seen from Fig. 4.11 that the creep rate increases with temperature and the three curves are roughly similar in shape. It is likely that three curves can be shifted horizontally to produce a smooth curve, suggesting TTSP method may be valid in analyzing creep compliance against logarithmic time property of SWCNT bundle at different temperatures.

Fig. 4.11 Creep compliance vs. time curves for SWCNT bundles at different temperatures, plotted based on a Burgers model using harmonic mean values of characteristic parameters obtained experimentally.

A smooth master curve at 23°C is produced only by horizontally shifting creep compliance curves at 38° and 54°C, as shown in Fig. 4.12, where iterative

refinement is made to maximize R-square value of the polynomial fit. The horizontal translations are first made between two curves for adjacent temperature levels. The shift factor, $\log(\alpha_t)$, for the curve at 54°C is obtained by accumulating two translations of one between two curves at 23°C and 38°C and the other between two curves at 38°C and 54°C.

In the shift of individual adjacent curves, a two-step iterative refinement technique is used. Consider two adjacent curves at 23° and 38°C. First, the curve at 38°C is shifted by a shift factor, $\log(\alpha_t)$, along the log (time) axis till a rough smooth curve is obtained. At the same time, the data points are fitted by a 6th order polynomial. Subsequently, a fine adjustment is made to the shift factor to maximize the R-square value of the polynomial fitting the data points. The optimum shift factor is determined to be 1.629. A similar procedure is also used for two curves at 38° and 54°C. It has been determined that the curve at 54°C need to be shifted by 0.273 to gain a smooth curve together with the curve at 38°C. So the shift factor for the curve at 54°C with a reference temperature of 23°C is calculated to be 1.902. The shift factors needed and the master curve produced are shown in Fig. 4.12. The master curve is finally fitted by a 6th order polynomial and the agreement is highly satisfactory with R-square of 0.9975. It is found from Fig. 4.12 that the master curve produced shows reverse curvature at about $10^{4.732}$ s (~15 hours) and two parts with different curvatures are annotated by arrows. Moreover, the longest time for the creep reaches $10^{6.634}$ s (~50 days), which can be used to predict long-time creep behavior of SWCNT bundle at low applied stress at 23 °C.

Fig. 4.12 Master curve of creep of SWCNT bundle after numerical refinement at a reference temperature of 23°C, showing reverse curvature at about 15 hours.

Some long-term time-dependent behaviors accomplished previously under static tension can be used to check the validity of this TTSP method. These tests were conducted at 23°C, which is the same as the reference temperature of the master curve. Three tensile creep compliance curves are plotted at constant applied stresses of 2.46 GPa, 3.94 GPa, and 4.07 GPa, respectively, together with the master curve, shown in Fig. 4.13. It is seen from the figure that tensile test curves and the master curve are similar within 10^4 s, however, a discrepancy occurs from 10^4 s, where the master curve shows reverse curvature. The reasons for the discrepancy are still to be further investigated.

Fig. 4.13 Tensile creep compliance curves plotted at three different constant applied stresses together with the master curve.

As described above, the shift factor is expected to obey the Arrhenius' Law since SWCNT bundles do not display a glass transition. Based on Eq. (4.3), the shift factor, $\log(\alpha_t)$, should be linear in terms of $1/T$. Three shift factors are plotted against $1/T$ in Fig. 4.14, which is fitted by a straight line with R-square of 0.724. The slope of the fit line of -5962.78 K is obtained. Therefore, the activation energy, Q , of the creep is calculated to be 114.17 kJ/mol using Eq. (4.3), independent of temperature, located in the lower value portion of a wide range of creep activation energy of graphite of 84-1047 kJ/mol [104]. The huge difference from 84 kJ/mol to 1047 kJ/mol is not due solely to structural difference between the various graphites under study by different researchers, but to a large extent to different methods of analysis employed [104]. The medium R-square value, 0.724, of the linear fit suggests the possibility of the validity of TTSP method for the creep compliance of SWCNT bundle.

However, none of the three data points just fell on the fitting straight line, which was probably attributed to simply experimental variation, but also possibly due to the difference of the activation energy at different temperatures. It is seen from Fig. 4.12 that the master curve shows reverse curvature between 10000 to 100000 s. This implies that there are possible different deformation mechanisms in different portions of the creep curve. Hence, it is necessary to add more test curves at different temperatures to check whether the activation energy is independent of temperature. As a result, a more accurate value of the activation energy will probably be calculated for better predicting creep behavior of SWCNT bundles and the validity of TTSP method will be confirmed.

Fig. 4.14 The shift factors, $\log(\alpha_t)$, plotted against $1/T$ and corresponding fitting straight line.

4.6 Conclusions

Our results show the patterns of S-N data and creep strain or compliance behaviors of SWCNT bundle at different temperatures. The S-N data show that fatigue

strength of SWCNT bundle at 38°C is obviously higher than that at 23°C but it is lowered when temperature reaches 54°C, suggesting that elevated temperature leads to strengthening or weakening of the structure of sample. The strengthening of the structure of sample could be attributed to possible hardening mechanisms, including continued graphitization, crack healing, changes in dislocation structure, and change of creep mechanism. When temperature is up to 54°C, elevated temperature might cause damage of the structure of sample, especially at higher applied stress. The creep strain or compliance behaviors of SWCNT bundles at 38° and 54°C can be modeled by a 4-element Burgers model. Elastic and viscous parameters for the model were found to decrease with increasing temperature. The creep compliance curves against logarithmic time at different temperatures were similar in shape and probably obeyed the TTSP principle. A master curve at 23°C was generated by simply horizontal shift of the curves along the log (time) axis. The shift factors obey the Arrhenius' Law. The activation energy of the creep process is estimated to be 114.17 kJ/mol. Creep data at more temperatures are needed to further confirm the validity of the TTSP method. At the same time, a more accurate value of activation energy is needed, to better predict creep behavior of SWCNT bundles at an arbitrary temperature using the master curve, for it is related to the creep mechanism.

CHAPTER 5

EFFECT OF DEFECTS AND INTER-DEFECT INTERACTION ON TIME-DEPENDENT FRACTURE BEHAVIOR OF A SWCNT UNDER STATIC TENSION

In previous chapters, studies on time-dependent behaviors of SWCNT bundle influenced by defects have been reviewed and presented. In this chapter, we will investigate how defects and inter-defect interaction influence time-dependent fracture behavior of a SWCNT under static tension at a molecular level.

A refined molecular life prediction scheme for SWCNTs, taking into consideration carbon-carbon bond rotation and preexisting strain under mechanical loads, is proposed. The time-dependent fracture behavior of 12 different cases of zigzag (18, 0) SWCNT, each without defects or embedded with either a single defect of different types or two interacting or non-interacting defects, is studied under axially constant tensile stress. It is shown that the patterns of atomistic crack propagation and fatigue lives of SWCNTs are influenced by the type and/or orientation of the defect(s), inter-defect distance, as well as the magnitude of externally applied stress. For SWCNTs with two defects, if the inter-defect distance is within the *indifference length*, defect-defect interaction does exist and it has pronounced effects on diminishing the lives of the nanotubes. Also, the defect-defect interaction is stronger at shorter inter-defect distance, resulting in shorter fatigue lives.

5.1 Introduction

As reviewed in Chapter 2, various mechanical properties or behaviors of CNTs are affected by defects within the nanotubes. Static fatigue strength of a SWCNT becomes lower and its life becomes shorter after a single SW defect is embedded in the SWCNT, based on a molecular life prediction scheme for time-dependent fracture behavior of SWCNTs [42, 91]. Stiffness, ultimate strength, and failure strain of CNTs are widely scattered as a result of defects, and the mean values of these mechanical properties decrease with increasing average number of defects [118]. Existence of more than one defect in a CNT may cause defect-defect interactions within a nanotube. Preliminary probe into the defect-defect interactions within a SWCNT has been conducted by Huq *et al.* [87, 88]. They have proposed that interaction of SW defects in a SWCNT is quantified by the magnitude of the energy of a “weak” C-C bond. The “weak” bond is the one with highest potential energy and is more prone to rupture than its neighboring bonds. It has been pointed out that the degree of defect interactions depends on defect type, inter-defect distance, and orientation of defects.

As mentioned in Chapters 3 and 4, sample variation significantly affects time-dependent behavior of SWCNT bundles at different temperatures, where defects are expected to play a dominant role in controlling the time-dependent behavior. Very little is known about how defects influence the time-dependent behavior of a CNT. In this chapter, the effect of defects and defect-defect interaction on time-dependent behavior of CNT is investigated. We utilize the concept developed earlier by Huq *et al.* to quantify the interactions of SW defects in a zigzag (18, 0) SWCNT under static axial tension. Based on a refined life prediction scheme for SWCNTs, fatigue lives of SWCNTs are determined and

patterns of atomistic crack propagations are demonstrated, and thus the influence of defect-defect interaction on fatigue behaviors of SWCNTs is revealed.

5.2 Theoretical background

The life prediction scheme for SWCNTs proposed previously is refined to predict the lifetime of SWCNTs with different defects and/or chirality taking into consideration bond rotation and preexisting strain. Previously [42], the scheme was proposed based on classical kinetic concept of solid fracture and a strain energy concentration concept. A C-C bond at the atomistic crack is considered when a SWCNT is stretched along the longitudinal axis from a zero stress state. The strain energy, u_i , of a C-C bond with highest bond energy, E , in a SWCNT is related to the axial tensile strain of the tube, ε , by [42]:

$$u_i = b_i \varepsilon^2 \quad (5.1)$$

where b_i is a coefficient in polynomial fitting of a u_i - ε curve, obtained by molecular mechanics simulations.

When defects exist in a SWCNT, the nanotube not only elongates but it also rotates as a whole in the process of tensile loading, so the C-C bond with E may be not be the one that is parallel to the longitudinal axis. Due to the existence of defects, the bond is pre-stressed and significantly longer than 0.142 nm [49], the stress-free bond length. Thus the preexisting strain energy of the C-C bond within a defect, u_{0i} , should also be taken into account. The strain energy of a C-C bond is more appropriately described by

$$u_i = b_i \varepsilon^2 + c_i \varepsilon + u_{0i} \quad (5.2)$$

where the second and third terms on the right hand side of Eq. (5.2) are related to the effects of bond rotation and preexisting strain, respectively. In the light of Zhurkov's dynamic fracture model [42, 90], the lifetime, t_i , of the i th C-C bond to be broken at the front of a crack with $i - 1$ broken bonds is [42]:

$$t_i = \tau_0 \exp\left(\frac{U_0 - u_i}{kT}\right) \quad (5.3)$$

where U_0 is the C-C bond dissociation energy, taken as 1.84×10^{-19} J/m², u_i represents the strain energy of the bond, τ_0 is the reciprocal fluctuation frequency of atoms, taken as 10^{-13} s, the Boltzmann constant k is 1.38×10^{-23} J/K and the absolute temperature T is 300K. Using molecular mechanics method, the total strain energy per atom, ξ_i , for a zigzag (18, 0) SWCNT with $i - 1$ broken bonds subjected to tensile load can be calculated, and the profile of ξ_i vs. ε can be obtained. By fitting the profile of ξ_i vs. ε , the total strain energy per atom, ξ_i , is approximately expressed by a quadratic function of axial tensile strain of a nanotube [119]:

$$\xi_i = \alpha_i \varepsilon^2 \quad (5.4)$$

The applied stress at the end of the SWCNT at small strains is [42]

$$\sigma = \frac{2\pi r}{A} \cdot \frac{\partial \xi_i}{\partial \varepsilon} = \frac{4\pi \alpha_i r}{A} \cdot \varepsilon \quad (5.5)$$

Where r and A are radius and cross-sectional area of the SWCNT, respectively. Because there is a lack of translational invariance in the radial direction, different cross-sectional areas are adopted for calculations. If some long individual SWCNTs are assembled into a bundle as shown in Fig. 5.1, and the bundle is treated as a solid ensemble, the cross-sectional area, A , of a SWCNT (in the bundle) is $\pi(r + h)^2$, where $2h$ is the gap between two adjacent SWCNTs.

The radius, r , is taken as 0.70 nm for zigzag (18, 0) tubes in all calculations and h is 0.34 nm, taken as the representative distance between two adjacent graphene layers [49].

Fig. 5.1 Schematic diagram of cross-sectional area of two SWCNTs in a bundle. Solid curves are SWCNTs with radius, r , and the area within a dash curve approximates cross-sectional area of a SWCNT, $\pi(r + h)^2$.

Thus Eq. (5.5) can be rewritten as

$$\sigma = \frac{4\alpha_i r}{(r+h)^2} \cdot \varepsilon \quad (5.6)$$

Substituting Eq. (5.6) into Eq. (5.2), we have

$$u_i = \gamma_i \sigma^2 + \delta_i \sigma + u_{0i} \quad (5.7)$$

where γ_i is the coefficient of strain energy concentration, and δ_i is a supplemental term pertinent to bond rotation. They read

$$\gamma_i = \frac{b_i \cdot (r+h)^4}{16\alpha_i^2 \cdot r^2}, \quad \delta_i = \frac{c_i \cdot (r+h)^2}{4\alpha_i \cdot r} \quad (5.8a, b)$$

Using these results in Eq. (5.3), at the front of an atomistic crack with $i - 1$ broken bonds, the lifetime, t_i , of the i th bond to be broken is

$$t_i = \tau_0 \exp\left(\frac{U_0 - \gamma_i \sigma^2 - \delta_i \sigma - u_{0i}}{kT}\right) \quad (5.9)$$

and the lifetime, t , of a SWCNT, is the sum of the lifetimes of all individual C-C bonds along the path of crack propagation

$$t = \sum_i t_i = \sum_i \tau_0 \exp\left(\frac{U_0 - \gamma_i \sigma^2 - \delta_i \sigma - u_{0i}}{kT}\right) \quad (5.10)$$

The three parameters, γ_i , δ_i , and u_{0i} , are related to “crack-tip” strain energy concentration, that can be obtained from molecular simulations. They are the only indispensable parameters required in calculating fatigue life of a SWCNT, and they need to be evaluated again for the new atomic crack geometry after a C-C bond has been broken.

5.3 Molecular modeling

Twelve molecular models of zigzag (18, 0) SWCNTs were constructed, shown in Fig. 5.2. Among them was a defect-free SWCNT and the other eleven tubes contain different defects, each embedded with either a single defect of different type, or a defect pair (either interacting or non-interacting). All the defects fall into five categories, namely, $A1$, $A2$, B , $A1-A2$ and $A1-B$ defects, and for either one of the $A1-A2$ and $A1-B$ defects, four configurations are involved according to the distance between two single defects, which are shown with dark-colored bonds in Fig. 5.2.

As far as defect configuration is concerned, $A1$ and $A2$ belong to the same type, consisting of pentagon-heptagon-heptagon-pentagon (5-7-7-5) rings arranged in

series (the line joining the two farthest apexes of the two pentagons is hereafter referred to as “orientation line”). For $A1$ defect, the orientation line is more or less perpendicular to the longitudinal axis of the SWCNT, while it is more or less parallel to the longitudinal axis for an $A2$ defect. In a B defect, the two pentagons are arranged on the two sides of two joining heptagons.

$A1$ - $A2$ (or $A1$ - B) defect is a defect pair, with a single $A1$ defect and a single $A2$ defect (or a single B defect) separated along the long axis of a SWCNT. For either one of the $A1$ - $A2$ and $A1$ - B defect pairs, four configurations were studied according to the distance between two single defects, D ; they are $A1$ - $A2/D_i$ ($i=0, 1, 2, 3$) and $A1$ - B/D_i ($i=0, 1, 2, 3$), respectively. Here the subscript denotes a specific distance. For example, $A1$ - $A2/D_1$ represents a defect-pair consisting of a single $A1$ defect and a single $A2$ defect separated by an inter-defect distance of D_1 . The shortest inter-defect distance, denoted by D_0 , indicates that two defects are joined side by side (shown in Fig. 5.2). On the basis of the configuration with D_0 inter-defect distance, defect pairs with discrete D_i can be constructed. The configurations of $A1$ - $A2/D_1$ and $A1$ - B/D_3 are shown in Fig. 5.2. It needs to be mentioned that D_i ($i=1, 2$, and 3) corresponding to the same subscript i may not be the same for different defect pairs; and the actual length of D_i are indicated in Fig. 5.3.

Fig. 5.2 Schematic molecular models of 12 zigzag (18, 0) SWCNTs without or with different types of SW defects: (a) no defect; (b) $A1$ defect; (c) $A2$ defect; (d) B defect; (e) $A1-A2/D_0$ defect; (f) $A1-A2/D_1$ defect; (g) $A1-A2/D_2$ defect; (h)

$A1-A2/D_3$ defect; (i) $A1-B/D_0$ defect; (j) $A1-B/D_1$ defect; (k) $A1-B/D_2$ defect; (l) $A1-B/D_3$ defect. Carbon-carbon bonds located in defects are highlighted by bold. The bond with highest bond energy, E , within each SWCNT is indicated by an arrow, which is the first C-C bond to be broken.

Molecular mechanics calculations were carried out using MM+ force field, an all atom force field. Geometry optimizations are performed using the Polak-Ribiere algorithm for the SWCNTs with defects at zero nominal strain, which means that they are fixed at the same length as that of a corresponding defect-free SWCNT at free-standing state. Due to the existence of defects, these SWCNTs are pre-stressed and some C-C bonds around the defect are rotated and strained, giving rise to higher bond energies than that in perfect hexagonal network. The bonds with the highest bond energy, E , in these SWCNTs are indicated by arrows in Fig. 5.2, which are the first bonds to be broken.

Geometry optimizations were performed for each SWCNT without broken bonds and after subsequent bond breaking events under different applied loads with nominal strains of 0-5%. Only the first nine or less (five for a SWCNT with $A2$ defect) crack geometries or bond breaking events were considered in this study, since subsequent bond rupture occur quickly and times-to-failure of these bonds are negligible. To start with, an intact SWCNT with no broken bonds is energetically optimized, and the C-C bond with highest energy, E , is detected to be the first bond to be broken. A “crack” is generated by manually eliminating the bond to be broken in the molecular model. Similarly, a “crack” with i ($i=2-9$) broken bonds is generated by manually erasing the bond to be broken upon the

crack geometry of the same SWCNT with $i - 1$ broken bonds based on energy considerations. It needs to be stated that only one bond breaking is considered at a time and simultaneous crack propagation in both defects is not considered in this work. The total strain energy per atom, ξ_i , for the entire nanotube and the strain energy, u_i , of a C-C bond with E are obtained for a crack geometry with $i - 1$ broken bonds at different nominal strains. Based on the life prediction scheme discussed in Section 5.2, the coefficients, α_i , b_i , c_i , and u_{0i} , are determined by fitting ξ_i vs. ε and u_i vs. ε curves. Using Eqs. (5.8a, b), three critical parameters, γ_i , δ_i , and u_{0i} are obtained and the lifetime of 12 SWCNTs (with and without defects) are calculated using Eqs. (5.9) and (5.10).

5.4 Results and discussion

5.4.1 The highest C-C bond energy

The highest C-C bond energy, E , for each of the 12 SWCNTs (with and without defects) at zero nominal strain, are shown in Fig. 5.3. They are denoted by 8 data points and 4 horizontal lines. E is plotted against inter-defect distance, D , for each of the 8 SWCNTs with either $A1-A2$ or $A1-B$ defect pair. For each of the other 4 SWCNTs with a single defect or no defect, the highest bond energy is presented as a horizontal line.

Fig. 5.3 Graphs of E (eV) of 12 zigzag (18, 0) SWCNTs of the same length with or without defects at zero nominal strain. 4 filled rectangles (■) denote E of 4 SWCNTs embedded with A1-B defect pairs from D_0 to D_3 ; 4 filled circles (●) denote E of 4 SWCNTs embedded with A1-A2 defect pairs from D_0 to D_3 ; The dotted lines linking up these data points indicate the trend of E with an increase of D . 4 horizontal lines represent E of SWCNTs with a single or no defect.

It is seen from Fig. 5.3 that the highest bond energy, E , in a defect-embedded SWCNT is evidently higher than that in a defect-free tube at the same zero nominal strains, suggesting that a defect might have some influence on the magnitude of E , and subsequently affecting the onset of initial bond breakage in the nanotube. Different defects may exert their influence to different extent. A1 defect leads to the largest E in all SWCNTs with single defects. For a SWCNT with a defect pair, E either increases or decreases monotonically with an increase

of inter-defect distance, depending on the type of defect pair involved. For an $A1-A2$ defect pair, E increases from 0.58 eV to 1.39 eV corresponding to an increase of inter-defect distance from D_0 to D_3 , and gradually approaches asymptotically the horizontal line of $E=1.43$ eV. However, for $A1-B$ defect pair, E decreases monotonically from 2.09 eV to 1.49 eV. Results presented in Fig. 5.3 illustrate defect-defect interactions in a SWCNT. The closer a defect pair is, the stronger the interaction between them. When separation between the two defects is big enough, beyond a so-called *indifference length*, which is about 3 nm [87], the interaction ceases. The interaction leads to an increase or a decrease in the E of a C-C bond, depending on the types of the defect pairs, and subsequently facilitates or restrains the onset of initial bond breakage of the nanotube. Influence of the defect interaction on the fatigue behavior of a SWCNT will be discussed in the following two sections.

5.4.2 Crack propagation

Through molecular mechanics calculations, crack propagations and stress-life (S-N) curves of all of 12 cases are simulated. For a defect-free SWCNT, the crack propagates along circumferential path on the SWCNT wall and the S-N curve shows much higher fatigue strength compared to those of SWCNTs with defects, which has been similarly reported [91]. In order to highlight the influence of different defects and inter-defect interactions on the time-dependent behavior of a SWCNT, simulated results of seven typical SWCNTs with either different types of defects or the same type but different inter-defect distances are presented and compared herein. They are those with single $A1$, $A2$, and B defects, and $A1-A2/D_0$, $A1-A2/D_1$, $A1-B/D_1$ and $A1-B/D_3$ defect-pairs.

Atomic-sized crack propagations for selected SWCNTs are listed in Fig. 5.4, where the chronological order of C-C bond breakage is illustrated by integers. It should be mentioned that the broken bonds are also the bonds with E , the highest bond energy. It is seen that different embedded defects and/or magnitudes of applied stress result in different crack propagation paths. $A1$ defect gives rise to a circumferential crack perpendicular to the long axis of the tube, while $A2$ defect causes crack to propagate along a helical path on the SWCNT wall. Crack propagation path for B defect depends on the magnitude of applied stress. When applied stress is higher than 6.3 GPa, it is circumferential, similar to that for $A1$ defect. Otherwise, the crack propagation path is spiral.

The phenomenon that crack propagation paths are dependent of applied stress is also embodied in SWCNTs with defect pairs. It is seen from Fig. 5.4 (e) - (l) that atom-sized cracks propagate perpendicularly to the long axis of the tubes at high stresses, while they move along helical paths at low stresses; for the latter, propagation in two defects are involved. For example, at higher stress (≥ 6.3 GPa), crack propagation stays within one defect (figures (i) and (k) in Fig. 5.4), while when the applied stress is lower than 6.5 GPa, crack propagation switches from one defect to another (for examples, figures (j) and (l) in Fig. 5.4).

Fig. 5.4 Schematics of propagation of atomic-sized crack on (18, 0) SWCNT embedded with single or defect-pair under high or low tensile stress. (a) A1 defect under full stress range; (b) A2 defect under full stress range; (c) B defect under high stress (≥ 6.3 GPa); (d) B defect under low stress (< 6.3 GPa); (e) A1-A2/D₁ defect-pair under high stress (≥ 7.2 GPa); (f) A1-A2/D₁ defect-pair under

low stress (<7.2 GPa); (g) $A1-A2/D_0$ ($D_0=0$) defect-pair under high stress (≥ 11.8 GPa); (h) $A1-A2/D_0$ ($D_0=0$) defect-pair ($D_0=0$) under low stress (<11.8 GPa); (i) $A1-B/D_3$ defect-pair under high stress (≥ 6.3 GPa); (j) $A1-B/D_3$ defect-pair under low stress (<6.3 GPa); (k) $A1-B/D_1$ defect-pair under high stress (≥ 6.5 GPa); (l) $A1-B/D_1$ defect-pair under low stress (<6.5 GPa).

5.4.3 Life prediction and comparison with experimental data

The computed S-N curves of the seven SWCNTs discussed earlier in previous section are obtained. For comparison, these seven S-N curves are divided into two groups and plotted in Figs. 5.5 and 5.6. One group is constituted by four S-N curves, named by Curves 1, 2, 3, and 4, corresponding to SWCNTs with $A1$, $A2$, $A1-A2/D_0$ and $A1-A2/D_1$, respectively (see Fig. 5.5). Curves 1 and 2 intersect at a point marked by a hollow circle, and in the middle of either of Curve 3 and 4 there is a sharp corner called “inflection point,” also marked by a hollow circle. The other group also consists of four S-N curves, corresponding to SWCNTs with $A1$, B , $A1-B/D_1$ and $A1-B/D_3$, i.e., Curves 1, 5, 6, and 7 (see Fig. 5.6). Similarly, the intersection of Curves 1 and 5, and the sharp turns on Curves 6 and 7 (inflection points), are all highlighted by hollow circles. Also included in both figures is a set of experimental S-N data of 37 SWCNT ropes from static fatigue testing [41].

Fig. 5.5 Four stress-life (S-N) curves of zigzag (18, 0) SWCNTs with $A1$, $A2$, $A1-A2/D_0$ and $A1-A2/D_1$, named by Curves 1, 2, 3, and 4, respectively. Hollow circles on the curves highlight inflection points or intersection. Solid circles are S-N data from static fatigue tests of SWCNT ropes [41].

It is seen from Fig. 5.5 that Curves 1 and 2 intersect at 6.5 GPa, which means that the SWCNT with a single $A1$ defect has shorter fatigue life than that with an $A2$ defect at stresses higher than 6.5 GPa, and the trend is reversed below 6.5 GPa. Curves 3 and 4 are located below Curves 1 and 2, with Curve 3 being the lowest of the four. The effect of inter-defect interactions between $A1$ and $A2$ is a discount of fatigue life of the nanotube compared to one with single defect, and the effect is more pronounced when the defects are closer to each other.

The inflection points on Curves 3 and 4 correspond to a stress of 11.8 and 7.2 GPa (referred to as “inflection stress” herein), respectively. Above the inflection stresses, Curves 3 and 4 are similar to Curve 1 in shape, except that they are more

or less translation towards the bottom left corner. Below the inflection stresses, Curves 3 and 4 resemble Curve 2 in shape. It is noted that the inflection stresses coincide with the stresses at which circumferential-to-spiral crack propagation transition occurs, as discussed in Section 5.4.2. Therefore, influence of applied stress on fatigue behavior of a SWCNT is reflected from the pattern of crack propagation and the S-N curve simultaneously. For a SWCNT with two interaction defects $A1$ and $A2$, $A1$ defect plays a dominating role in the fatigue behavior above the inflection stress while $A2$ defect takes the leading role below the inflection stress.

Such changes in time-dependent behaviors of SWCNTs can be interpreted in terms of bond energy. Here we take a SWCNT with $A1$ - $A2/D_1$ as an example, referring to results presented in Fig. 5.4 (e, f) and Curve 4 in Fig. 5.5. Results from Fig. 5.4 (a, b) and Curves 1 and 2 in Fig. 5.5 may serve as comparison. When applied stress is above the inflection stress (7.2 GPa), it is found from Fig. 5.4 (e) that the first broken C-C bond occurs on $A1$ defect (labeled by integer 1). Subsequently, more C-C bond breaking occurs around $A1$ defect due to locally high strain energy (chronologically labeled by integers 3-9), tracing out a circumferential pattern of crack path. At this time, most of bonds around $A2$ defect are not broken because of relatively lower C-C bond energies. The crack geometry is similar to one with a single $A1$ defect (see Fig. 5.4 (a)).

The corresponding section of the S-N curve, i.e., the section above the inflection point of Curve 4, nearly coincides with Curve 1 (see Fig. 5.5). Here the existence of a nearby $A2$ defect only slightly boosts C-C bond energies around the $A1$ defect and causes stronger local energy to speed up the fracture process in $A1$ defect. However, when the applied stress is below the inflection stress, it is found from Fig. 5.4 (f) that other C-C bonds around $A1$ defect are more stable, after the first

three C-C bond rupture (labeled by integers 1, 3, and 4). On the other hand, C-C bonds around $A2$ defect become less stable, and start to propagate along a helical path, similar to that with a single $A2$ defect (see Fig. 5.4 (b)). Incidentally, the corresponding section of the S-N curve (Curve 4, the section below the inflection point) is similar to Curve 2 in shape (see Fig. 5.5).

Similarly, it is found from Fig. 5.6 that Curves 1 and 5 intersect at 8.1 GPa; and Curves 6 and 7 are nearly located below Curves 1 and 5, with Curve 6 the lowest. It is seen from the results that the SWCNT with a single $A1$ defect has shorter fatigue life than one with a single B defect at stresses higher than 8.1 GPa, and the trend is reversed below 8.1 GPa. In SWCNTs with $A1-B$ defects, inter-defect interaction is also in effect, diminishing the fatigue lives of the nanotubes. The detrimental effect to fatigue life becomes more pronounced at shorter inter-defect distance. Inflection points on Curves 6 and 7 correspond to stresses of 6.5 GPa and 6.3 GPa (referred to as “inflection stress” herein), respectively. Above the inflection stresses, Curves 6 and 7 are similar to Curve 1 in shape, while they are close to Curve 5 below the inflection stresses. The inflection stresses are in fact the stresses where pattern of crack propagation changes from circumferential to spiral. So in view of the shape of S-N curves and crack propagation with $A1-B$ defects, $A1$ defect plays a dominating role above the inflection stresses, and B defect does the opposite. The energy interpretation of the S-N curve would be similar to previous discussion on the SWCNT with an $A1-A2/D_1$ defect.

Fig. 5.6 Four stress-life (S-N) curves of zigzag (18, 0) SWCNTs with $A1$, B , $A1-B/D_1$ and $A1-B/D_3$, named by Curves 1, 5, 6 and 7 respectively. Hollow circles on the curves highlight inflection points of curves or intersection of both curves. Solid circles are S-N data from static fatigue tests of SWCNT ropes [41].

In essence, the crack propagation paths in SWCNTs may vary depending on the type and/or orientation of embedded defects, as well as the magnitude of applied stress, and that has profound influence on their fatigue lives. When inter-defect distance is beyond the *indifference length*, one defect does not feel the existence of the other. For these cases, no interaction exists and crack propagation path and fatigue life of the SWCNT is anticipated to be the same as those with a single defect.

It is seen from Fig. 5.5 and Fig. 5.6 that majority of experimental S-N data tend to cluster along simulated S-N curves for a SWCNT with a defect pair, suggesting that there might be more than one defects in the SWCNT bundles that are dominating their lives. It should be noted that the S-N curves simulated differ

from experimental results, because the simulation is only for a single SWCNT while the tests are conducted on some SWCNT bundles.

5.5 Conclusions

A refined life prediction scheme for SWCNT is presented, taking rotation and preexisting strain of the C-C bonds into consideration. Atomic-sized crack propagations and S-N curves of SWCNTs with different single defects and defect pairs are studied. For a SWCNT with a single *A1* defect, its crack is always circumferential at high stress and its fatigue life is the shortest among those with a single defect. A SWCNT with a single *A2* or *B* defect has shorter fatigue life only at low stress. *A2* defect gives rise to spiral crack, while *B* defect causes either circumferential crack at high stress or spiral crack at low stress. For SWCNTs with *A1-A2* or *A1-B* defects, crack propagation paths and S-N curves tend to those of SWCNTs with a single *A1* defect at high stress, while at low stress they approach those with *A2* or *B* defect. We have shown that defect interaction does exert detrimental effect on the fatigue lives of SWCNTs, the shorter the inter-defect distance, the stronger their influence.

CHAPTER 6

TIME-DEPENDENT BEHAVIOR OF SWCNT/EPOXY COMPOSITE UNDER STATIC TENSION

Time-dependent behaviors of SWCNT bundle under static tension have been investigated systematically in the previous chapters. In this chapter, we study the time-dependent behavior and fracture mechanisms of SWCNT rope reinforced epoxy composite (hereafter referred to as SWCNT/epoxy composite) under static tension at room temperature.

Creep tests are performed for SWCNT/epoxy composite and neat epoxy samples. Based on experimental results, a 4-element Burgers model [97] is introduced to describe their viscoelastic behaviors. In the same way of SWCNT bundle obtained in Chapter 3, creep compliance of SWCNT/epoxy composite and neat epoxy are also obtained. The relationship of creep characteristics between SWCNT/epoxy composite and its constituents is constructed, from which creep compliance of SWCNT/epoxy composite is deduced. Moreover, stress-life (S-N) data of SWCNT/epoxy composite and neat epoxy, as well as S-N data of SWCNT bundle in the composite and the stand-alone SWCNT bundle, are obtained and compared. Finally, fatigue fracture surface of SWCNT/epoxy composite are observed through FESEM and possible failure mechanisms of the composite are revealed.

6.1 Experiments

Twenty-nine SWCNT/epoxy composites and forty-two neat epoxy samples were fabricated and tested (in which failure occurred within the “gauge region”) in an Instron 8800 Micro-Force Tester with a static load cell with a capacity of 100 N. Specimen fabrication and testing procedures are described as follows.

6.1.1 Specimen fabrication

SWCNT/epoxy composite specimens were fabricated manually for static fatigue testing. Neat epoxy resin samples of the same size were also produced for comparison. The materials were SWCNT rope as a reinforcement and Epicote 1006 epoxy resin system as a matrix. As mentioned in Chapter 2, the SWCNT ropes used in this study were synthesized by a catalytic decomposition of hydrocarbon, and consisted of long, aligned SWCNT bundles, each with length ranged from 20 to 40 mm and diameter in the range of 10 to 40 nm [70, 71]. The density of the SWCNT is 1.138 g/cm^3 [70]. Epicote 1006 epoxy resin system, used as the matrix of SWCNT/epoxy composites and the only material of neat epoxy samples, was supplied by Yen International Resources Pte. Ltd (Singapore). It was a combination of liquid bisphenol-A, epichlorohydrin epoxide resin, amine (resin) and polymeric additives (hardener). The Epicote 1006 epoxy resin system has a density of 1.11 g/cm^3 and can be properly cured at room temperature with a ratio of epoxy resin to hardener of 5:3 by weight, as given by the supplier. Knowing the densities of the SWCNT and the epoxy matrix, the volume fraction of SWCNT in composites can be calculated from its weight fraction, which is easy to measure and to control.

Referring to the schematic diagram of specimen processing flowchart in Fig. 6.1 on page 103, SWCNT/epoxy composite samples are fabricated in the following steps.

- (i) A 70×30 mm rectangular hard paper with a dog-bone shaped outline was pasted using adhesive tape and fixed on a large glass plate. The adhesive tape was used to ease the composite cured to be separated from the paper substrate. The outline on the substrate acted as a reference in the processing of composites, such as placing nanotube bundles and cutting into a dog-bone shaped sample. The dimensions of the outline are shown in Fig. 6.2, among which the dog-bone shaped geometry is about 50 mm in length (16 mm gauge length) and 2.5 mm in width. At the same time, two 1 mm thick glass slides were adhered to two sides of the hard paper on the same large glass plate. As a result, a groove with about 0.5 mm in depth was formed, in which SWCNT/epoxy composites or neat epoxy samples can be casted.
- (ii) The epoxy resin system was prepared by mixing epoxy resin and hardener with the ratio of 5:3 by weight. The epoxy resin and hardener were allowed to flow down, along a glass rod, into a bottle, and were gently stirred to minimize the possibility of air bubbles becoming trapped within the mixture. A thin layer of epoxy was evenly brushed onto the surface of the pre-pasted hard paper. A 20 mm long SWCNT rope was separated carefully from a thicker SWCNT ropes and weighed in advance. The SWCNT rope prepared was picked up, aligned by a slight tension using two sharp tweezers and quickly laid onto the thin layer of epoxy.

- (iii) More epoxy matrix was poured and then excessive epoxy was mopped gently. The composite sheet formed had a thickness of about 0.3-0.6 mm, determined by the glass groove.
- (iv) After 72 hours curing at room temperature, the composite sheet was cut into a dog-bone shaped composite specimen in a digital control milling machine along the embedded baseline on the hard paper substrate.
- (v) Finally, sand paper was used to polish the edges of the specimen to reduce the possibility of the failures caused by stress concentration in edges. Sand paper strips were bonded to the ends of the specimen to facilitate gripping. At the same time, the sand paper was marked with sample number. Neat epoxy resin specimens of the same dimensions were also produced by the similar procedures, without SWCNT ropes embedded.

Fig. 6.1 A flowchart of fabrication of SWCNT/epoxy composite.

Fig. 6.2 Dog-bone shaped outline on a paper substrate.

Since the epoxy system would be cured at room temperature, sample casting need be finished within 30 minutes. Otherwise the resin would be hard to handle because of increased viscosity. In practice, only 3-6 samples were fabricated every time and classified into a specific batch. All samples were numbered with the uniform format of the character “Comp” or “R” connected with ‘Integer 1_Integer 2’, where ‘Comp’ and ‘R’ denote SWCNT/epoxy composite and neat epoxy resin sample, respectively, and “Integer 1” denotes number of batch and “Integer 2” denotes number of sample. For instance, such two numbers as “Comp15_2” and “R2_3” represent the second SWCNT/epoxy composite in Batch 15 and the third neat epoxy resin sample in Batch 3, respectively.

Two typical batches of SWCNT/epoxy composites and neat epoxy samples are shown in Fig. 6.3. In the figure, neat epoxy samples are pasted with sand papers at the two ends, while SWCNT/epoxy composites are not, so as to reveal the CNT rope embedded.

Fig. 6.3 Typical samples for fatigue testing: (a) SWCNT/epoxy composites without sand papers pasted and (b) neat epoxy samples with sand papers pasted at two ends of the samples.

6.1.2 Testing procedure

Seventy-one successful tensile tests (in which failure occurred within the 16 mm long gauge region) were carried out at room temperature on an Instron™ 8800 micro-force testing system with a static load cell of 100 N capacity. The samples include 29 SWCNT/epoxy composites and 42 neat epoxy samples. A photo of the whole testing setup is shown in Fig. 6.4. Sample was mounted on the testing machine tightly through a special clamp, which can be seen from the close-up in Fig. 6.4. Built-in software for Instron 8800 system, *FastTrack 2*, was used to control the testing system and record real-time data.

Fig. 6.4 An Instron™ 8800 micro-force testing system for static fatigue tests. Inset is the close-up.

There are two phases in the loading history: a quasi-static ramp, followed by a constant load. In the ramp phase, the speed of the cross-head of the clamp is 5×10^{-5} m/s. When force reaches the pre-determined value, displacement control is changed into load control. The test is now in static fatigue phase which means entering static fatigue phase with a constant applied force until presupposed enough long time (7 days) or failure. According to failure times of the samples, the samples are divided into three classes: the first is “Quasi-static tension” in which they failed in the ramp process, the second is “Static fatigue” in which they failed during the second phase of static fatigue, and the third is “Survivor” where they survived static fatigue within a stipulated time.

6.2 Determination of volume fraction of constituents of SWCNT/epoxy

The volume fraction of the constituents of SWCNT/epoxy composites was determined indirectly. First, the segment of the composite containing SWCNT ropes was cut and measured from fractured SWCNT/epoxy sample, after a tensile test was finished. Since the weight of embedded SWCNT rope was measured in advance, the weight fraction of SWCNT can be calculated for the gauge segment of the composite. Knowing the densities of SWCNT and epoxy matrix, 1.138 g/cm³ and 1.11 g/cm³, respectively, as well as 2% effective SWCNT bundle in SWCNT rope by volume as described in Section 3.4.1, the volume fractions of the SWCNTs, the SWCNT bundle and the epoxy matrix can be calculated.

Supposing that W denotes weight fraction of the SWCNT bundle in SWCNT/epoxy composite, and V^{cnt} denotes volume fraction of the SWCNT bundle in the composite, the latter can be calculated according to the following formulation:

$$V^{cnt} = \left(\frac{W}{1.138} \right) / \left(\frac{W}{1.138 \times 2\%} + \frac{1-W}{1.11} \right) \quad (6.1)$$

Thus, the volume fraction of SWCNT rope (including inter-SWCNT bundle spacing) is $50V^{cnt}$ according to 2% effective SWCNT bundle in SWCNT rope by volume. Except for the SWCNT bundle, the remaining space of $49V^{cnt}$ within a SWCNT rope cannot undergo any loads and is considered as void. So the volume fraction of the epoxy matrix, V^e , is

$$V^e = 1 - 50V^{cnt} \quad (6.2)$$

6.3 A model for creep in SWCNT/epoxy composite

The 4-element Burgers model was also used to characterize the creep behavior of SWCNT/epoxy composite and neat epoxy samples. First, creep strain-time curves obtained experimentally were fitted by the basic equation of 4-element Burgers model (Eq. (3.8)), to obtain two sets of four characteristic elastic and viscous parameters, which corresponded to SWCNT/epoxy composites and neat epoxy samples, respectively. Subsequently, each set of the four characteristic parameters were averaged in harmonic mean method. Finally, four characteristic parameters of the material were used to plot creep compliance vs. time curves, indicating creep property of the material, independent of external applied stress. The method or technique for the data processing and analysis was described in detail in Section 3.3.

Based on the Burgers model, the creep compliance of SWCNT/epoxy composite can be obtained by the creep tests and theoretical derivation from creep tests of their constituents, SWCNT bundle and neat epoxy. First, a schematic diagram of SWCNT/epoxy composite was given according to the volume fractions of its constituents, as shown in Fig. 6.5. Volume fraction of each constituent was annotated in parentheses in the figure, following the name of the constituent. In the figure there are three main constituents in SWCNT/epoxy composite, i.e., SWCNT bundle, void, and epoxy. The SWCNT bundle and void constitute the SWCNT rope. The volume fractions of the SWCNT bundle and the epoxy matrix are annotated by V^{cnt} and V^e , and for void and the SWCNT rope, the volume fractions are annotated by the expressions of $49V^{cnt}$ and $50V^{cnt}$, based on 2% effective SWCNT bundle in real SWCNT rope mentioned in Section 3.4.1.

Fig. 6.5 A schematic diagram of SWCNT/epoxy composite showing volume fractions of its constituents.

On the basis of the composition of the SWCNT/epoxy composite shown in Fig. 6.5 and uniaxial tension in creep, we hypothesize that the creep of SWCNT/epoxy composite can be modeled by a combination of both 4-element Burgers models for the SWCNT and neat epoxy models in parallel (hereafter referred to as “*composite*” Burgers model), except for a common 4-element Burgers model. The two models for the creep of SWCNT/epoxy composite are shown in Fig. 6.6, where superscripts, cnt , e , and c , denote characteristic parameters for the SWCNT, neat epoxy and SWCNT/epoxy composite, respectively.

Fig. 6.6 Two equivalent models for creep of SWCNT/epoxy composite: (a) 4-element Burgers model and (b) “*composite*” Burgers model containing two Burgers models for the SWCNT bundle and neat epoxy models connected in parallel.

For a SWCNT/epoxy composite under a constant applied stress, σ , the induced creep strain, ε , is time-dependent. When a Burgers model, as shown in Fig. 6.6 (a), is used, we have

$$\varepsilon^c = \frac{\sigma^c}{E_1^c} + \frac{\sigma^c}{E_2^c} \left(1 - e^{-\frac{E_2^c}{\eta_2^c} t} \right) + \frac{\sigma^c}{\eta_3^c} t \quad (6.3)$$

$$\sigma^c = \sigma \quad (6.4)$$

$$\varepsilon^c = \varepsilon \quad (6.5)$$

However, when a “*composite*” Burgers model, as shown in Fig. 6.6 (b), is employed, we have the following:

$$\varepsilon^{cnt} = \frac{\sigma^{cnt}}{E_1^{cnt}} + \frac{\sigma^{cnt}}{E_2^{cnt}} \left(1 - e^{-\frac{E_2^{cnt}}{\eta_2^{cnt}} t} \right) + \frac{\sigma^{cnt}}{\eta_3^{cnt}} t \quad (6.6)$$

$$\varepsilon^e = \frac{\sigma^e}{E_1^e} + \frac{\sigma^e}{E_2^e} \left(1 - e^{-\frac{E_2^e}{\eta_2^e} t} \right) + \frac{\sigma^e}{\eta_3^e} t \quad (6.7)$$

$$\sigma^{cnt} V^{cnt} + \sigma^e V^e = \sigma \quad (6.8)$$

$$\varepsilon^{cnt} = \varepsilon^e = \varepsilon \quad (6.9)$$

Here, σ^{cnt} and ε^{cnt} , and σ^e and ε^e represent stress and strain of the SWCNT and epoxy, of the composite in a “*composite*” Burgers model, respectively. From Eqs. (6.3) - (6.9), a relationship of creep characteristic parameters of the composite and its constituents can be approximately derived based on reasonable hypothesis (see Appendix IV for detailed mathematical derivations):

$$E_1^c = E_1^{cnt} V^{cnt} + E_1^e V^e \quad (6.10)$$

$$\eta_3^c = \eta_3^{cnt} V^{cnt} + \eta_3^e V^e \quad (6.11)$$

$$\eta_2^c = 1 / \left[\left(\frac{1}{\eta_2^{cnt}} + \frac{1}{\eta_3^{cnt}} \right) / \left(V^{cnt} + \frac{1/\eta_2^{cnt} + 1/\eta_3^{cnt}}{1/\eta_2^e + 1/\eta_3^e} \right) - \frac{1}{\eta_3^{cnt} V^{cnt} + \eta_3^e V^e} \right] \quad (6.12)$$

$$E_2^c = (\eta_2^c)^2 / \left[\frac{(\eta_2^{cnt})^2}{E_2^{cnt}} \cdot V^{cnt} + \frac{(\eta_2^e)^2}{E_2^e} \cdot V^e \right] \quad (6.13)$$

Equations (6.10) - (6.13) can be used to predict creep behaviors of the composites with varying ratios of the constituents within a moderate range only if the creep characteristic parameters of the constituents are known. More importantly, they could be used to offer theoretic guidance for designing different SWCNT/epoxy composite to meet the requirement of creep deformation.

6.4 Results and discussion

Results of 15 tests for each kind of SWCNT/epoxy composites and neat epoxy samples, with clear creep characteristics, are selected to analyze creep behaviors of the corresponding material. The volume fractions of the SWCNT in SWCNT/epoxy composites are calculated. Creep compliances of two constituent materials of SWCNT/epoxy composites and neat epoxy are obtained experimentally. At the same time, for SWCNT/epoxy composites, it is also predicted theoretically, which agrees with experimental results almost perfectly. Furthermore, S-N data for SWCNT/epoxy composites and neat epoxy samples are plotted and compared. And S-N data for the SWCNT in the composites are obtained and compared with that of stand-alone SWCNT rope obtained previously. Finally, fracture morphologies for the composites are presented and analyzed.

6.4.1 Volume fraction of the constituents of composite

All SWCNT/epoxy composite samples are weighed and weight fractions of the SWCNT are calculated, with the average value of 0.3%. For the 15 selected composite samples, their weights of SWCNTs and the samples, as well as weight fractions of SWCNT, are summarized in Appendix V. It is seen that weight fraction of the SWCNT in the composites ranges from 0.1% to 0.7% and with an average of 0.3%. The variability of SWCNT volume fraction among the samples would cause the diversity of resulting characteristic parameters from individual creep curves. Thus, the final characteristic parameters for the composite are obtained by calculating harmonic mean values of characteristic parameters of individual samples. Referring to Eqs. (6.1) - (6.2), since the value of W is 0.3%, the values of V^{cnt} and V^e are calculated to be 0.3% and 85%, which is used in

the prediction of creep behavior of the composite based on a “*composite*” Burgers model in Section 6.4.2.

6.4.2 Creep compliance of SWCNT/epoxy and neat epoxy

Three typical creep strain vs. time curves for SWCNT/epoxy composites obtained experimentally are plotted during constant load stage and fitted by the Burgers model, as shown in Fig. 6.7. Accordingly, four characteristic parameters, E_1 , E_2 , η_2 , and η_3 , for each SWCNT/epoxy composite sample were obtained. It is seen from Fig. 6.7 that the fitted curves are in very good agreement with experimental data, indicating that the Burgers model can be used to characterize the creep behavior of SWCNT/epoxy composite. All four characteristic parameters for 15 selected composite samples are listed in Appendix VI. Based on Eq.(3.20), the four characteristic parameters are averaged to be as those for the material of SWCNT/epoxy with such the constituents as 15% SWCNT rope (0.3% SWCNT bundle) and 85% epoxy in volume. Corresponding quantities are 2109 MPa, 10627 MPa, 7.5×10^6 MPa·s, and 3.92×10^7 MPa·s, as are also included in Appendix VI.

With the four values, a creep compliance vs. time curve is plotted in Fig. 6.8 based on Eq. (3.11), presented by a dash line. The curve represents creep characteristics of the composite material, independent of external applied stress, with an exception of minor influence of the variability among samples on the test result. It was found that the derivative of creep compliance of the composite with respect to time is about 2.6×10^{-8} MPa⁻¹·s⁻¹ at steady stage, i.e., the strain rate is constant with increasing time and in proportion to applied stress.

Fig. 6.7 Typical experimental and fitted creep curves of SWCNT/epoxy composites by the Burgers model under different stresses. The value of applied stress of each sample is annotated in parentheses.

Fig. 6.8 Creep compliance, J , plotted against time for SWCNT/epoxy composite and neat epoxy based on a Burgers model: two sets of harmonic means of all corresponding characteristic parameters obtained experimentally are used (refer to Appendixes VI and VII).

Similarly, three typical creep strain vs. time curves for neat epoxy samples under different stresses obtained experimentally are plotted and fitted by the Burgers model, as shown in Fig. 6.9. The Burgers model is checked to be suitable for characterizing creep behaviors of neat epoxy samples. The characteristic parameters obtained and their harmonic means for 15 neat epoxy samples based on the model are summarized listed in Appendix VII.

Using four harmonic mean characteristic parameters of neat epoxy samples, 1971 MPa, 11935 MPa, 7.21×10^6 MPa·s and 3.2×10^7 MPa·s, a creep compliance curve for the neat epoxy material was also plotted in Fig. 6.8 based on Eq. (3.11), presented by a solid line. The curve represented creep characteristics of the neat epoxy material on average. It was seen from Fig. 6.8 that the compliance value at zero time of the neat epoxy curve was higher than that of the curve of SWCNT/epoxy, and at longer time the slope of the epoxy curve was 3.1×10^{-8} MPa⁻¹·s⁻¹, higher than corresponding quantity of SWCNT/epoxy (2.6×10^{-8} MPa⁻¹·s⁻¹). This indicates that the addition of the SWCNT rope gave rise to a slight reduction in the deformation and creep rate of the epoxy composite, which will be interpreted in the next sections.

Fig. 6.9 Typical experimental and fitted creep curves of neat epoxy samples by the Burgers model under different stresses. The value of applied stress of each sample is annotated in parentheses.

Using the relationships derived for characteristic parameters of the SWCNT/epoxy composite and its constituents, Eqs. (6.10)-(6.13), four characteristic parameters, E_1^c , E_2^c , η_2^c , and η_3^c , can be deduced from two sets of harmonic mean characteristic parameters for neat epoxy and the stand-alone SWCNTs obtained experimentally. Harmonic mean values of the four characteristic parameters for neat epoxy were given in the previous paragraph. Values for stand-alone SWCNT bundle can be found in Section 3.4.2. Together with the values of V^{cnt} and V^e of 0.3% and 85% calculated in 6.4.1, four characteristic parameters for the SWCNT/epoxy were predicted and compared with aforementioned experimental results, as shown in Table 6.1. It is seen from Table 6.1 that two sets of data are in excellent agreement. From two compliance curves plotted with the two sets of data, it is obvious that the two curves matched almost perfectly. Thus the validity of “*composite*” Burgers model for composite material in creep

and the relationship derived of characteristic parameters between the composite and its constituents for predicting creep behavior of the composite is verified. Meanwhile, a minor improvement of SWCNT/epoxy composite in creep-resistance compared to neat epoxy sample may be attributed to the existence of amount of void in SWCNT/epoxy composite. So it is required to fully disperse the SWCNT bundles within a SWCNT rope into the matrix to reduce volume fraction of void in the composite. What is more, the “*composite*” Burgers model and the relationship derived could be used to offer theoretic guidance for improving creep property of SWCNT/epoxy composite and designing specific SWCNT/epoxy composite to meet the requirement of creep deformation. More importantly, this idea could probably be applied to other composites in creep for predicting creep behaviors of the composites with specific compositions.

Table 6.1 The predicted and experimental values for elastic and viscous parameters for the composite.

Calculated values	$E_1(10^2\text{MPa})$	$E_2(10^2\text{MPa})$	$\eta_2(10^6\text{MPa-s})$	$\eta_3(10^6\text{MPa-s})$
Predicted	21.37	101.36	6.83	39.37
Experimental	21.09	106.27	7.50	39.19

Fig. 6.10 Creep compliance, J , plotted against time for SWCNT/epoxy composite based on the Burgers model: the four parameters predicted and harmonic means of corresponding experimental quantities (Appendix VI) are used respectively.

6.4.3 S-N curves of SWCNT/epoxy and neat epoxy

S-N plots of 29 SWCNT/epoxy composites and 42 neat epoxy samples under tension are shown in Fig. 6.11. In the figure, three types of symbols, stars, circles and triangles, denote “Quasi-static tension”, “Static fatigue”, and “Survivor”, respectively; solid and hollow symbols represent SWCNT/epoxy composites and neat epoxy samples respectively. Based on Eq. (3.21), “static fatigue” data of SWCNT/epoxy composites and neat epoxy samples are fitted by straight lines with R-square values of 0.832 and 0.233, respectively, indicated by solid and dash lines in Fig. 6.11, respectively. It is found from the two R-square values that static fatigue of the SWCNT/epoxy composite has a typical linear normalized S-N curve while that of neat epoxy has not. The more apparent scattering in data of neat

epoxy samples may be attributed to stronger influence of air bubbles in samples on fatigue behavior of neat epoxy samples than of the composites. It is calculated from the fitted straight lines based on Eq. (3.21) that ultimate stress, σ_{ult} , and the slope of the normalized S-N curve, m , for the SWCNT/epoxy composites are 51.39 MPa and 0.097, respectively, and corresponding quantities for neat epoxy are 42.47 MPa and 0.082, respectively. It is found that the time-to-failure for SWCNT/epoxy composite with only 0.3% SWCNT in volume is obviously longer than that of the neat epoxy under static fatigue, indicating that static fatigue life of neat epoxy can be improved by adding SWCNT bundles to form SWCNT/epoxy composite.

Fig. 6.11 Stress-life (S-N) comparison of SWCNT/epoxy composites and neat epoxy samples under static fatigue.

6.4.4 S-N curves of SWCNTs in composites

Since the volume fraction of SWCNT bundle varies from sample to sample, applied stress of SWCNT bundle, instead of the stress of composite, is plotted against the time-to-failure of the composite. Using an equal strain rule of mixture for unidirectional fiber composite [86], the stress of SWCNT bundle in the composite was estimated:

$$\sigma_{cnt} = \frac{E_{cnt}}{E_c} \cdot \sigma_c \quad (6.14)$$

Where σ_{cnt} and σ_c are the stress of SWCNT bundle and of the composite, respectively, and E_{cnt} and E_c are the Young's modulus of SWCNT bundle and of the composite, respectively. In order to calculate the stress in SWCNT, E_c was measured by tensile test prior to fatigue test. The values of E_c varies due to the variation of volume content of CNT in epoxy composites. E_{cnt} was taken as Young's modulus value of 540 GPa. Hence, applied stresses of SWCNT were calculated for corresponding lifetime for all composites.

S-N data of SWCNT bundles in composites are plotted in Fig. 6.12. Based on Eq. (3.21), "static fatigue" data are fitted by straight lines with R-square values of 0.845, showing static fatigue of SWCNT bundles in the composite has a typical linear normalized S-N curve. Also included in Fig. 6.12 are S-N plots of the stand-alone SWCNT bundles from Section 3.4.2 for comparison. It is seen that the fitted lines of the two S-N curves in Fig. 6.12 cross at 7.2 GPa. In view of logarithmic coordinates of time in the abscissa, the static fatigue life of SWCNTs in SWCNT/epoxy composite is similar to or slightly shorter than that of the stand-alone SWCNT bundles at higher applied stresses, and it is much longer at lower applied stresses. The phenomenon can be partly attributed to load transfer

from the epoxy matrix to the SWCNT bundles in the composite, and effect of stepped fracture that SWCNT bundles in a rope do not fracture simultaneously, where the remaining SWCNTs undergo increasing stress in a SWCNT rope during creep when a bundle or subbundle failure has occurred.

Fig. 6.12 Stress-life (S-N) comparison of SWCNT bundles in SWCNT/epoxy composites and stand-alone SWCNT bundles under static fatigue.

6.4.5 Fracture morphology analysis

The morphologies of the fracture surfaces of SWCNT/epoxy composites were examined by FESEM. Typical FESEM images of the fatigue fracture topographies of SWCNT/epoxy composites are shown in Figs. 6.13-6.17.

On the left hand region of Fig. 6.13, where no SWCNT bundles are embedded in the epoxy, a flat, brittle-like fracture surface is evidently seen, and on the right hand side numerous fractures and splitting of SWCNT bundles are observed near

the roots of SWCNTs. SWCNT splitting within a bundle is usually believed to be attributed to the difference in interactions between outer-layer SWCNTs of the bundle and the epoxy matrix, and inter-tubular interaction. Most SWCNTs of outer layer are observed to have fractured, leaving behind some very short fractured nanotubes (about hundreds of nanometers), as can be easily seen from the figure and more clearly from Fig. 6.14. It is also found from fracture surfaces of these fractured SWCNTs that the peripheral SWCNT bundles are fully immersed in the epoxy matrix. This suggests good wetting of SWCNTs with epoxy matrix and strong adhesion between them, agreeing reasonably well with experimental evidence that load transfer exists from the SWCNTs to the matrix in the composite. However, those SWCNTs surrounded by the outer-layer SWCNTs prefer to be split into thinner bundles rather than fracture directly due to high tensile strength of SWCNT and the difference in interactions between outer-layer SWCNTs of the bundle and the epoxy matrix, and inter-tubular interaction. Since the split SWCNTs are located at the inner layer of a SWCNT rope and do not touch the epoxy matrix directly, interfacial bonding between split SWCNTs and the epoxy matrix does not exist. As the splitting and sub-splitting of SWCNTs have accumulated, weaker sub-split SWCNTs gradually fracture and eventually the split SWCNTs are pulled out from the matrix to form a specific morphology.

Fig. 6.13 A FESEM image of fracture surface of SWCNT/epoxy composite, showing flat featherless fracture surface on the region where the epoxy contains no CNT reinforcement and numerous fractures and splitting of CNT bundles on the CNT-embedded epoxy.

Fig. 6.14 A FESEM image of fracture surface of SWCNT/epoxy composite, showing numerous fractures and splitting of CNT bundles on the CNT-embedded epoxy, happened close to the root of CNT bundles embedded in the matrix.

The fracture tip (see Fig. 6.15) displays tree-branch feature and rather flat brittle-like fracture surfaces, which are indicated by a circle in Fig. 6.15 and can be seen clearly from a higher magnification FESEM image in Fig. 6.16. Away from the fractured tip SWCNTs bundle is split extensively and at the region close to the SWCNT embedded matrix it is anchored firmly on the epoxy matrix in the way that some branches of a tree root originated from splitting of SWCNT bundle are partially exposed outside the ground.

Fig. 6.15 A FESEM image of fracture surface of SWCNT/epoxy composite, showing numerous fractures and splitting of CNT bundles on the CNT-embedded epoxy, happened at the very fracture tip.

Fig. 6.16 A high magnification FESEM image of fracture surface of SWCNT/epoxy composite, showing many fractures and splitting of CNT bundles on the CNT-embedded epoxy, happened at the very fracture tip.

On the longitudinal surface of SWCNT bundle/epoxy composite, as shown in Fig. 6.16, stretching and splitting of some long SWCNT bundles and many short fractured SWCNTs can be seen. It is expected that the long SWCNT bundles will be pulled out from the matrix, once the short split subbundles connected with the matrix fracture. In order to utilize the exceptional mechanical properties of SWCNT bundle, therefore, sufficient separation of SWCNT bundle and complete dispersion into the matrix are very crucial to produce an effective composite material.

Fig. 6.17 A longitudinal surface of a broken SWCNT/epoxy composite also showing numerous fractures and splitting of CNT bundles on the CNT-embedded epoxy.

6.5 Conclusions

Our results show that a 4-element Burgers model can be used to characterize the creep behaviors of SWCNT/epoxy composites and neat epoxy samples. A “composite” Burgers model is proposed to characterize creep behavior of SWCNT/epoxy composites via characteristic parameters of its constituents, SWCNT and neat epoxy. The relationship has been constructed between the characteristic parameters for SWCNT/epoxy composite and its constituents. It can be used to predict the viscoelastic behavior of SWCNT/epoxy composites with different fractions of SWCNTs and to offer a theoretical guidance in the mixture ratio for designing a composite with a specified viscoelastic property.

Creep resistance and static fatigue life of neat epoxy can be significantly improved by adding SWCNT bundles to form SWCNT/epoxy composite. Even though there is only slight difference in between at higher applied stresses, the static fatigue life of SWCNTs in SWCNT/epoxy composite is much longer than that of the stand-alone SWCNT bundles at lower applied stresses. This is believed to be attributed to load transfer from the epoxy matrix to the SWCNT bundles in the composite, and the fact that the stand-alone SWCNT bundles are under increasing stress under long-term static fatigue when subbundle failures have occurred.

The fatigue fracture surfaces of SWCNT bundles, through FESEM observations, illustrated that SWCNTs bundle failed subsequently at a subbundle level, with splitting and brittle fractures of SWCNT subbundles. Due to local load sharing mechanisms, many subbundles fractures are approximately in the same location of a bundle to form a flat brittle-like fracture surface on some subbundles. FESEM examination for SWCNT/epoxy composite offered some evidence that possible failure mechanisms of SWCNTs in composite are fracture of single SWCNTs, splitting of SWCNT bundle and pullout of subbundles from the matrix.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

With the aim to exploit the unique mechanical properties of CNTs for high-performance composite materials, we have carried out extensive studies on time-dependent behaviors and fracture mechanisms of aligned SWCNT bundles under static tension at room temperature, the influences of temperature on the time-dependent behaviors of the SWCNT bundles, the influence of defects embedded on the time-dependent behaviors of a SWCNT under static tension, and time-dependent behaviors and fracture mechanisms of SWCNT/epoxy composites under static tension using experimental methods and molecular level simulations. In the following, results achieved to date are outlined.

1) Time-dependent behavior of SWCNT bundle under static tension at room temperature

We have performed tensile tests of SWCNT rope at room temperature under constant applied stress. Stress-life (S-N) data and creep strain vs. time curves have been obtained experimentally to better characterize the time-dependent behavior of SWCNT bundle at room temperature. The S-N data show a typical linear normalized S-N curve for static fatigue of SWCNT bundle. The fatigue strengths of SWCNT bundle are doubled within 10^4 s and similar at longer time, compared with that of graphite fiber. The fatigue limits of SWCNT bundles seem to exist at 4-5 GPa within the time scale of 48 hours. The creep strain vs. time

curves can be well fitted by a 4-element Burgers model. Four characteristic parameters for each sample have been obtained by fitting the creep strain vs. time curve obtained experimentally. However, the four parameters measured experimentally are influenced by sample variation and different applied stress. And the degree of influence by sample variation is similar or higher than that by applied stress. A quadrilinear stress-dependent strain rate relation is proposed to discuss the complicate dependence of creep mechanism on applied stress. Creep mechanism is difficult to be simply determined by stress exponent, and it is controlled by defects in samples. Based on a hypothesis that the four parameters are independent of applied stress, the harmonic means of characteristic parameters of all samples in tests are calculated to wash out the effect of sample variation and “noise” in experimental data. An average creep compliance behavior of SWCNT bundles at the applied stress in the range of 3.24-13.89 GPa is obtained, presenting the applied stress-independent creep compliance behavior on a whole. The steady-state strain rate is in proportion to applied stress and the ratio is about $8.2 \times 10^{-8} \text{ GPa}^{-1} \cdot \text{s}^{-1}$.

Morphologies of fracture surfaces of SWCNT bundles have also been observed through FESEM examination. The results show that fractures occur at a subbundle level, with splitting and numerous brittle fractures of SWCNT subbundles. SWCNT bundles fracture stepwise at different locations, probably due to the difference in locations of defects distributed along the SWCNTs. This coincides with the defect-controlling creep behavior of SWCNT rope at room temperature obtained by Burgers model analysis.

2) *Effect of temperature on time-dependent behavior of SWCNT bundle under static tension*

The patterns of S-N data and creep strain or compliance behaviors of SWCNT bundle at three different temperatures (23°, 38° and 54°C) have been presented. The S-N data show that fatigue strength of SWCNT bundle at 38°C is obviously higher than that at 23°C but it is lowered when temperature reaches 54°C, suggesting that elevated temperature leads to strengthening or weakening of the structure of sample. The strengthening of the structure of sample could be attributed to possible hardening mechanisms, including continued graphitization, crack healing, changes in dislocation structure, and change of creep mechanism. When temperature is up to 54°C, elevated temperature might cause damage of the structure of sample, especially at higher applied stress.

The creep strain or compliance behaviors of SWCNT bundles at 38° and 54°C can be modeled by a 4-element Burgers model. Four characteristic parameters for the model were found to decrease with increasing temperature. The creep compliance curves against logarithmic time at different temperatures were similar in shape and probably obeyed the time-temperature superposition (TTSP) principle. A master curve at 23°C was generated by simple horizontal shift of the curves along the log (time) axis, which may be used to predict creep behavior of SWCNT bundles at an arbitrary temperature. The shift factors obey Arrhenius' Law. The activation energy of the creep process is estimated to be 114.17 kJ/mol.

3) Effect of defects and inter-defect interaction on time-dependent fracture behavior of a SWCNT under static tension

Taking rotation and preexisting strain of the C-C bonds into consideration, a refined life prediction scheme for SWCNT has been proposed. Atomic-sized crack propagations and S-N curves of 12 SWCNTs with different single defect and defect pair are obtained. For a SWCNT with a single A1 defect, its crack is

always circumferential at high stress and its fatigue life is the shortest among those with a single defect. A SWCNT with a single *A2* or *B* defect has shorter fatigue life only at low stress. *A2* defect gives rise to spiral crack, while *B* defect causes either circumferential crack at high stress or spiral crack at low stress. For SWCNTs with *A1-A2* or *A1-B* defects, crack propagation paths and S-N curves tend to those of SWCNTs with a single *A1* defect at high stress, while at low stress they approach those with *A2* or *B* defect. Therefore, defect interaction does exert detrimental effect on the fatigue lives of SWCNTs, and the shorter inter-defect distance leads to the stronger influence.

4) Time-dependent behavior of SWCNT/ epoxy composite under static tension

The creep behaviors of SWCNT/epoxy composites and neat epoxy samples have been checked to be able to be characterized by a 4-element Burgers model. A “composite” Burgers model is proposed to characterize creep behavior of SWCNT/epoxy composites via characteristic parameters of its constituents, SWCNT and neat epoxy. The relationship has been constructed between the characteristic parameters for SWCNT/epoxy composite and its constituents, which can well predict the viscoelastic behavior of SWCNT/epoxy composites with different fraction of SWCNTs and even to apply to other composites.

Creep resistance and static fatigue life of neat epoxy can be significantly improved by adding SWCNT bundles to form SWCNT/epoxy composite. Even though there is only slight difference in between at higher applied stresses, the static fatigue life of SWCNTs in SWCNT/epoxy composite is much longer than that of the stand-alone SWCNT bundles at lower applied stresses. This is believed to be attributed to load transfer from the epoxy matrix to the SWCNT bundles in the

composite, and the fact that the stand-alone SWCNT bundles are under increasing stress under long-term static fatigue when subbundle failures have occurred.

The fatigue fracture surfaces of SWCNT bundles, through FESEM observations, illustrated that SWCNTs bundle failed subsequently at a subbundle level, with splitting and brittle fractures of SWCNT subbundles. Due to local load sharing mechanisms, many subbundles fractures are approximately in the same location of a bundle to form a flat brittle-like fracture surface on some subbundles. FESEM examination for SWCNT/epoxy composite offered some evidence that possible failure mechanisms of SWCNTs in composite are fracture of single SWCNTs, splitting of SWCNT bundle and pullout of subbundles from the matrix.

7.2 Recommendations

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

1) Creep mechanisms of SWCNT bundle at different temperatures

Due to temperature change of SWCNT bundles, the phenomenon of strengthening or weakening of the structure of sample appears. Moreover, the reverse curvature in the creep master curve implies that possible different mechanisms are involved at different portions of the creep curve. In order to resolve this matter, a further study on activation energy for creep is necessary. More creep curves at a wider spectrum of test temperatures are expected to determine whether the activation energy depends on temperature, to confirm the validity of TTSP method. It probably involves the improvement in heat insulation of ready-made experimental devices, making sure that the temperature on the bottom of the output tube of force transducer is always below 60°C when the temperature of a sample connected with

the tip of the output tube is higher. Also, a more accurate value of the activation energy can be calculated for better predicting creep behavior of SWCNT bundles.

2) Modelling of time-dependent behavior of SWCNTs with different defect assemblies

Since the influence of defect interaction on time-dependent behavior of a SWCNT has been presented, it is expected that a further molecular simulation on time-dependent behavior of a SWCNT with different defect assemblies will be conducted. For the cases with the same number of defects, statistical analysis will be applied to obtain mean values and deviations of time-to-failure for every stresses, and a band-shaped S-N diagram for SWCNTs with the specific number of defects can be plotted. Among the cases with different numbers of defects, some band-shaped S-N diagrams for different number defects will be compared and an asymptotic distribution of time-to-failure of a defective SWCNT with increasing number of defects could be obtained, which may predict the influence of defect number on the time-dependent behavior of a SWCNT.

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APPENDIXES

Appendix I: The four characteristic parameters for 13 SWCNT bundles at 23°C modelled by a 4-element Burgers model and their harmonic mean values.

Sample No.	$E_1(10^2\text{GPa})$	$E_2(10^2\text{GPa})$	$\eta_2 (10^6\text{GPa}\cdot\text{s})$	$\eta_3 (10^6\text{GPa}\cdot\text{s})$
T23-11	5.41	8.91	14.25	162.00
T23-89	3.98	3.70	0.32	50.22
T23-40	4.26	8.41	1.13	11.95
T23-37	5.65	6.67	0.97	4.65
T23-104	2.24	8.06	2.97	64.56
T23-56	5.16	12.44	1.78	9.97
T23-4	5.05	25.06	25.96	754.00
T23-41	3.63	3.18	0.45	794.00
T23-2	5.76	8.57	0.76	7.56
T23-110	6.12	29.64	0.83	5.70
T23-30	8.65	12.67	0.40	3.92
T23-10	4.96	40.42	2.85	30.03
T23-70	5.06	19.64	0.89	34.73
Harmonic mean	4.62	8.58	0.88	12.17

Appendix II: Experimental determined elastic and viscous parameters for 7 selected SWCNT ropes at 38°C modeled by a Burgers model and their harmonic mean values.

Sample No.	$E_1(10^2\text{GPa})$	$E_2(10^2\text{GPa})$	$\eta_2 (10^6\text{GPa}\cdot\text{s})$	$\eta_3 (10^6\text{GPa}\cdot\text{s})$
T38-54	2.13	0.91	0.06	6.44
T38-70	3.16	5.75	0.04	1.55
T38-56	4.32	4.36	0.25	4.99
T38-52	5.03	1.01	0.10	15.65
T38-51	4.59	1.49	0.12	13.14
T38-55	4.38	28.35	0.35	1.39
T38-74	6.86	5.62	0.17	21.56
Harmonic mean	3.87	2.07	0.10	3.67

Appendix III: Experimental determined elastic and viscous parameters for 7 selected SWCNT ropes at 54°C modeled by a 4-element Burgers model and their harmonic mean values.

Sample No.	$E_1(10^2\text{GPa})$	$E_2(10^2\text{GPa})$	$\eta_2 (10^6\text{GPa}\cdot\text{s})$	$\eta_3 (10^6\text{GPa}\cdot\text{s})$
T54-91	6.55	1.15	0.05	201.41
T54-96	4.54	0.96	0.03	32.46
T54-93	3.00	4.00	0.35	16.83
T54-92	4.99	3.24	0.07	0.39
T54-95	6.84	1.05	0.03	10.08
T54-76	2.51	2.07	0.32	22.23
T54-84	1.67	2.18	0.17	25.59
Harmonic mean	3.42	1.60	0.06	2.45

Appendix IV: Mathematical derivation of relationship of creep characteristic parameters of SWCNT/epoxy composite and its constituents based on the Burgers model.

Referring to Fig. 6.6, at any time, we have:

$$\varepsilon^{cnt} = \frac{\sigma^{cnt}}{E_1^{cnt}} + \frac{\sigma^{cnt}}{E_2^{cnt}} \left(1 - \exp^{-\frac{E_2^{cnt}}{\eta_2^{cnt}} t} \right) + \frac{\sigma^{cnt}}{\eta_3^{cnt}} \cdot t \quad (\text{A.1})$$

$$\varepsilon^e = \frac{\sigma^e}{E_1^e} + \frac{\sigma^e}{E_2^e} \left(1 - \exp^{-\frac{E_2^e}{\eta_2^e} t} \right) + \frac{\sigma^e}{\eta_3^e} \cdot t \quad (\text{A.2})$$

$$\varepsilon^c = \frac{\sigma^c}{E_1^c} + \frac{\sigma^c}{E_2^c} \left(1 - \exp^{-\frac{E_2^c}{\eta_2^c} t} \right) + \frac{\sigma^c}{\eta_3^c} \cdot t \quad (\text{A.3})$$

$$\sigma = \sigma^c = \sigma^{cnt} \cdot V^{cnt} + \sigma^e \cdot V^e \quad (\text{A.4})$$

At $t = 0$, no relative motions should exist between CNT bundle and epoxy in a composite, therefore:

$$\varepsilon = \frac{\sigma^{cnt}}{E_1^{cnt}} = \frac{\sigma^e}{E_1^e} = \frac{\sigma^c}{E_1^c}, \text{ at } t = 0. \quad (\text{A.5})$$

From Eqs. (A.4) and (A.5), we have:

$$E_1^c = E_1^{cnt} \cdot V^{cnt} + E_1^e \cdot V^e \quad (\text{A.6})$$

Since $\sigma^c = \sigma^{cnt} \cdot V^{cnt} + \sigma^e \cdot V^e = \text{const}$, therefore

$$\dot{\sigma}^c = \dot{\sigma}^{cnt} \cdot V^{cnt} + \dot{\sigma}^e \cdot V^e = 0 \quad (\text{A.7})$$

$$\ddot{\sigma}^c = \ddot{\sigma}^{cnt} \cdot V^{cnt} + \ddot{\sigma}^e \cdot V^e = 0 \quad (\text{A.8})$$

where dot and double dot on the applied stress of the composite, σ^c , denote first

derivative and second derivative of σ^c in terms of time, respectively, i.e., $\dot{\sigma}^c = \frac{d\sigma^c}{dt}$ and $\ddot{\sigma}^c = \frac{d^2(\sigma^c)}{dt^2}$. Dot and double dot on an arbitrary physical quantity have similar definition in the following derivations.

From Eq. (A.4), we get:

$$\sigma^e = \frac{\sigma^c - \sigma^{cnt} \cdot v^{cnt}}{v^e} \quad (\text{A.9})$$

From Eq. (A.7), we get:

$$\dot{\sigma}^e = -\frac{\dot{\sigma}^{cnt} \cdot v^{cnt}}{v^e} \quad (\text{A.10})$$

and from Eq. (A.8), we get:

$$\ddot{\sigma}^e = -\frac{\ddot{\sigma}^{cnt} \cdot v^{cnt}}{v^e} \quad (\text{A.11})$$

Through taking first derivative of Eq. (A.1) in terms of time, we have:

$$\dot{\varepsilon}^{cnt} = \frac{\dot{\sigma}^{cnt}}{E_1^{cnt}} + \frac{\dot{\sigma}^{cnt}}{E_2^{cnt}} \left(1 - \exp^{-\frac{E_2^{cnt}}{\eta_2^{cnt}} t} \right) + \frac{\sigma^{cnt}}{\eta_2^{cnt}} \cdot \exp^{-\frac{E_2^{cnt}}{\eta_2^{cnt}} t} + \frac{\sigma^{cnt}}{\eta_3^{cnt}} + \frac{\dot{\sigma}^{cnt}}{\eta_3^{cnt}} \cdot t \quad (\text{A.12})$$

Similarly, by taking first derivative of Eqs. (A.2) and (A.3), we have:

$$\dot{\varepsilon}^e = \frac{\dot{\sigma}^e}{E_1^e} + \frac{\dot{\sigma}^e}{E_2^e} \left(1 - \exp^{-\frac{E_2^e}{\eta_2^e} t} \right) + \frac{\sigma^e}{\eta_2^e} \cdot \exp^{-\frac{E_2^e}{\eta_2^e} t} + \frac{\sigma^e}{\eta_3^e} + \frac{\dot{\sigma}^e}{\eta_3^e} \cdot t \quad (\text{A.13})$$

$$\dot{\varepsilon}^c = \frac{\dot{\sigma}^c}{E_1^c} + \frac{\dot{\sigma}^c}{E_2^c} \left(1 - \exp^{-\frac{E_2^c}{\eta_2^c} t} \right) + \frac{\sigma^c}{\eta_2^c} \cdot \exp^{-\frac{E_2^c}{\eta_2^c} t} + \frac{\sigma^c}{\eta_3^c} + \frac{\dot{\sigma}^c}{\eta_3^c} \cdot t \quad (\text{A.14})$$

Substitute $\dot{\sigma}^c = 0$ into Eq. (A.14):

$$\dot{\varepsilon}^c = \frac{\sigma^c}{\eta_2^c} \cdot \exp^{-\frac{E_2^c}{\eta_2^c} t} + \frac{\sigma^c}{\eta_3^c} \quad (\text{A.15})$$

Substitute Eqs. (A.9) and (A.10) into Eq. (A.13):

$$\begin{aligned}\dot{\xi}^e = & -\frac{\dot{\sigma}^{cnt} \cdot V^{cnt}}{V^e \cdot E_1^e} - \frac{\dot{\sigma}^{cnt} \cdot V^{cnt}}{V^e \cdot E_2^e} \left(1 - \exp^{-\frac{E_2^e}{\eta_2^e} t}\right) + \frac{\sigma^c - \sigma^{cnt} \cdot V^{cnt}}{V^e \cdot \eta_2^e} \cdot \exp^{-\frac{E_2^e}{\eta_2^e} t} + \\ & \frac{\sigma^c - \sigma^{cnt} \cdot V^{cnt}}{V^e \cdot \eta_3^e} - \frac{\dot{\sigma}^{cnt} \cdot V^{cnt}}{V^e \cdot \eta_3^e} \cdot t\end{aligned}\quad (A.16)$$

By taking second derivative of Eq. (A.1) in terms of time, we have:

$$\begin{aligned}\ddot{\xi}^{cnt} = & \frac{\ddot{\sigma}^{cnt}}{E_1^{cnt}} + \frac{\ddot{\sigma}^{cnt}}{E_2^{cnt}} \left(1 - \exp^{-\frac{E_2^{cnt}}{\eta_2^{cnt}} t}\right) + \frac{\ddot{\sigma}^{cnt}}{\eta_3^{cnt}} \cdot t + \frac{2\dot{\sigma}^{cnt}}{\eta_2^{cnt}} \cdot \exp^{-\frac{E_2^{cnt}}{\eta_2^{cnt}} t} + \frac{2\dot{\sigma}^{cnt}}{\eta_3^{cnt}} - \\ & \frac{\sigma^{cnt} \cdot E_2^{cnt}}{(\eta_2^{cnt})^2} \cdot \exp^{-\frac{E_2^{cnt}}{\eta_2^{cnt}} t}\end{aligned}\quad (A.17)$$

Similarly, by taking second derivative of Eqs. (A.2) and (A.3), we have:

$$\begin{aligned}\ddot{\xi}^e = & \frac{\ddot{\sigma}^e}{E_1^e} + \frac{\ddot{\sigma}^e}{E_2^e} \left(1 - \exp^{-\frac{E_2^e}{\eta_2^e} t}\right) + \frac{\ddot{\sigma}^e}{\eta_3^e} \cdot t + \frac{2\dot{\sigma}^e}{\eta_2^e} \cdot \exp^{-\frac{E_2^e}{\eta_2^e} t} + \frac{2\dot{\sigma}^e}{\eta_3^e} - \frac{\sigma^e \cdot E_2^e}{(\eta_2^e)^2} \exp^{-\frac{E_2^e}{\eta_2^e} t}\end{aligned}\quad (A.18)$$

$$\begin{aligned}\ddot{\xi}^c = & \frac{\ddot{\sigma}^c}{E_1^c} + \frac{\ddot{\sigma}^c}{E_2^c} \left(1 - \exp^{-\frac{E_2^c}{\eta_2^c} t}\right) + \frac{\ddot{\sigma}^c}{\eta_3^c} \cdot t + \frac{2\dot{\sigma}^c}{\eta_2^c} \cdot \exp^{-\frac{E_2^c}{\eta_2^c} t} + \frac{2\dot{\sigma}^c}{\eta_3^c} - \frac{\sigma^c \cdot E_2^c}{(\eta_2^c)^2} \exp^{-\frac{E_2^c}{\eta_2^c} t}\end{aligned}\quad (A.19)$$

Substitute $\dot{\sigma}^c = 0$, and $\ddot{\sigma}^c = 0$ into Eq. (A.19):

$$\ddot{\xi}^c = -\frac{\sigma^c \cdot E_2^c}{(\eta_2^c)^2} \cdot \exp^{-\frac{E_2^c}{\eta_2^c} t}\quad (A.20)$$

Substitute Eqs. ((A.9)–(A.11)) into Eq. (A.18):

$$\ddot{\xi}^e = -\frac{\ddot{\sigma}^{cnt} \cdot V^{cnt}}{V^e \cdot E_1^e} - \frac{\ddot{\sigma}^{cnt} \cdot V^{cnt}}{V^e \cdot E_2^e} \left(1 - \exp^{-\frac{E_2^e}{\eta_2^e} t}\right) - \frac{\ddot{\sigma}^{cnt} \cdot V^{cnt}}{V^e \cdot \eta_3^e} \cdot t$$

$$-2 \frac{\dot{\sigma}^{cnt} \cdot V^{cnt}}{V^e \cdot \eta_2^e} \cdot \exp^{-\frac{E_2^e}{\eta_2^e} t} - 2 \frac{\dot{\sigma}^{cnt} \cdot V^{cnt}}{V^e \cdot \eta_3^e} - \frac{(\sigma^c - \sigma^{cnt} \cdot V^{cnt}) \cdot E_2^e}{V^e \cdot (\eta_2^e)^2} \cdot \exp^{-\frac{E_2^e}{\eta_2^e} t} \quad (A.21)$$

For an intact SWCNT/epoxy composite under loading, we can assume that there are no relative motions all along or stress transfer initially between CNT bundle and the epoxy matrix. Therefore,

At $t \in [0, \infty)$, ε^c , ε^{cnt} , and ε^e are continuously differentiable, and there are:

$$\dot{\varepsilon}^c = \dot{\varepsilon}^{cnt} = \dot{\varepsilon}^e \quad (A.22)$$

$$\ddot{\varepsilon}^c = \ddot{\varepsilon}^{cnt} = \ddot{\varepsilon}^e \quad (A.23)$$

And at $t = 0$,

$$\dot{\sigma}^{cnt} = \ddot{\sigma}^{cnt} = 0 \quad (A.24)$$

I.e.,

$$\begin{aligned} \dot{\varepsilon} &= \frac{\sigma^c}{\eta_2^c} \cdot \exp^{-\frac{E_2^c}{\eta_2^c} t} + \frac{\sigma^c}{\eta_3^c} \\ &= \frac{\dot{\sigma}^{cnt}}{E_1^{cnt}} + \frac{\dot{\sigma}^{cnt}}{E_2^{cnt}} \left(1 - \exp^{-\frac{E_2^{cnt}}{\eta_2^{cnt}} t}\right) + \frac{\sigma^{cnt}}{\eta_2^{cnt}} \cdot \exp^{-\frac{E_2^{cnt}}{\eta_2^{cnt}} t} + \frac{\sigma^{cnt}}{\eta_3^{cnt}} + \frac{\dot{\sigma}^{cnt}}{\eta_3^{cnt}} \cdot t \\ &= -\frac{\dot{\sigma}^{cnt} \cdot V^{cnt}}{V^e \cdot E_1^e} - \frac{\dot{\sigma}^{cnt} \cdot V^{cnt}}{V^e \cdot E_2^e} \left(1 - \exp^{-\frac{E_2^e}{\eta_2^e} t}\right) + \frac{\sigma^c - \sigma^{cnt} \cdot V^{cnt}}{V^e \cdot \eta_2^e} \cdot \exp^{-\frac{E_2^e}{\eta_2^e} t} \\ &\quad + \frac{\sigma^c - \sigma^{cnt} \cdot V^{cnt}}{V^e \cdot \eta_3^e} - \frac{\dot{\sigma}^{cnt} \cdot V^{cnt}}{V^e \cdot \eta_3^e} \cdot t \end{aligned} \quad (A.25)$$

$$\text{And, } \ddot{\varepsilon} = -\frac{\sigma^c \cdot E_2^c}{(\eta_2^c)^2} \cdot \exp^{-\frac{E_2^c}{\eta_2^c} t}$$

$$= \frac{\ddot{\sigma}^{cnt}}{E_1^{cnt}} + \frac{\ddot{\sigma}^{cnt}}{E_2^{cnt}} \left(1 - \exp^{-\frac{E_2^{cnt}}{\eta_2^{cnt}} t}\right) + \frac{\ddot{\sigma}^{cnt}}{\eta_3^{cnt}} \cdot t + \frac{2\dot{\sigma}^{cnt}}{\eta_2^{cnt}} \cdot \exp^{-\frac{E_2^{cnt}}{\eta_2^{cnt}} t} + \frac{2\dot{\sigma}^{cnt}}{\eta_3^{cnt}} -$$

$$\begin{aligned}
 & \frac{\sigma^{cnt, E_2^{cnt}}}{(\eta_2^{cnt})^2} \cdot \exp^{-\frac{E_2^{cnt}}{\eta_2^{cnt}} t} \\
 &= -\frac{\ddot{\sigma}^{cnt, V^{cnt}}}{V^e \cdot E_1^e} - \frac{\ddot{\sigma}^{cnt, V^{cnt}}}{V^e \cdot E_2^e} \left(1 - \exp^{-\frac{E_2^e}{\eta_2^e} t}\right) - \frac{\ddot{\sigma}^{cnt, V^{cnt}}}{V^e \cdot \eta_3^e} \cdot t - 2 \frac{\dot{\sigma}^{cnt, V^{cnt}}}{V^e \cdot \eta_2^e} \cdot \exp^{-\frac{E_2^e}{\eta_2^e} t} - \\
 & \quad 2 \frac{\dot{\sigma}^{cnt, V^{cnt}}}{V^e \cdot \eta_3^e} - \frac{(\sigma^c - \sigma^{cnt, V^{cnt}}) \cdot E_2^e}{V^e \cdot (\eta_2^e)^2} \cdot \exp^{-\frac{E_2^e}{\eta_2^e} t}
 \end{aligned} \tag{A.26}$$

When the creep exceeds the transient time from primary to secondary creep, t_{tran} , Eq. (A.25) becomes:

$$\dot{\varepsilon}^c = \frac{\sigma^c}{\eta_3^c} = \frac{\sigma^{cnt}}{\eta_3^{cnt}} = \frac{\sigma^c - \sigma^{cnt, V^{cnt}}}{V^e \cdot \eta_3^e} \tag{A.27}$$

Here, for simplicity, $\dot{\sigma}^{cnt} = 0$, and $\dot{\sigma}^{cnt} \cdot t = 0$ are assumed at $t \gg t_{tran}$.

From Eq. (A.27), we have got

$$\eta_3^c = \eta_3^{cnt} \cdot V^{cnt} + \eta_3^e \cdot V^e \tag{A.28}$$

At $t = 0$, substitute Eq. (A.24) into Eq. (A.25), we have

$$\begin{aligned}
 \dot{\varepsilon}^c &= \sigma^c \cdot \left(\frac{1}{\eta_2^c} + \frac{1}{\eta_3^c}\right) = \sigma^{cnt} \cdot \left(\frac{1}{\eta_2^{cnt}} + \frac{1}{\eta_3^{cnt}}\right) = (\sigma^c - \sigma^{cnt, V^{cnt}}) \cdot \left(\frac{1}{V^e \cdot \eta_2^e} + \right. \\
 & \quad \left. \frac{1}{V^e \cdot \eta_3^e}\right)
 \end{aligned} \tag{A.29}$$

From Eqs. (A.28) and (A.29), we have got

$$\eta_2^c = 1 / \left[\left(\frac{1}{\eta_2^{cnt}} + \frac{1}{\eta_3^{cnt}} \right) / \left(V^{cnt} + \frac{1/\eta_2^{cnt} + 1/\eta_3^{cnt}}{1/\eta_2^e + 1/\eta_3^e} \cdot V^e \right) - \left(\frac{1}{\eta_3^{cnt, V^{cnt}}} + \frac{1}{\eta_3^e \cdot V^e} \right) \right] \tag{A.30}$$

At $t = 0$, substitute Eq. (A.24) into Eq. (A.26), we have

$$\ddot{\varepsilon} = -\frac{\sigma^c \cdot E_2^c}{(\eta_2^c)^2} = -\frac{\sigma^{cnt, E_2^{cnt}}}{(\eta_2^{cnt})^2} = -\frac{(\sigma^c - \sigma^{cnt, V^{cnt}}) \cdot E_2^e}{V^e \cdot (\eta_2^e)^2} \tag{A.31}$$

From Eq. (A.31), we have got

$$\frac{(\eta_2^c)^2}{E_2^c} = \frac{(\eta_2^{cnt})^2 \cdot V^{cnt}}{E_2^{cnt}} + \frac{(\eta_2^e)^2 \cdot V^e}{E_2^e}$$

So,

$$E_2^c = (\eta_2^c)^2 / \left[\frac{(\eta_2^{cnt})^2 \cdot V^{cnt}}{E_2^{cnt}} + \frac{(\eta_2^e)^2 \cdot V^e}{E_2^e} \right] \quad (\text{A.32})$$

In conclusion, the relationships of creep characteristic parameters of SWCNT/epoxy composite and its constituents are obtained, which are represented by Eqs. (A.6), (A.28), (A.30) and (A.32) and shown as follows.

$$\left\{ \begin{array}{l} E_1^c = E_1^{cnt} V^{cnt} + E_1^e V^e \\ \eta_3^c = \eta_3^{cnt} V^{cnt} + \eta_3^e V^e \\ \eta_2^c = 1 / \left[\left(\frac{1}{\eta_2^{cnt}} + \frac{1}{\eta_3^{cnt}} \right) / \left(V^{cnt} + \frac{1/\eta_2^{cnt} + 1/\eta_3^{cnt}}{1/\eta_2^e + 1/\eta_3^e} \right) - \frac{1}{\eta_3^{cnt} V^{cnt} + \eta_3^e V^e} \right] \\ E_2^c = (\eta_2^c)^2 / \left[\frac{(\eta_2^{cnt})^2}{E_2^{cnt}} \cdot V^{cnt} + \frac{(\eta_2^e)^2}{E_2^e} \cdot V^e \right] \end{array} \right. \quad (\text{A.33})$$

Appendix V: Components of 15 SWCNT/epoxy composites

Sample No.	Weight of SWCNT bundle (mg)	Weight of SWCNT/epoxy composite (g)	wt% of SWCNT bundle (%)
Comp15_2	0.057	0.033	0.2
Comp10_1	0.137	0.029	0.5
Comp13_2	0.155	0.048	0.3
Comp13_1	0.070	0.028	0.2
Comp10_4	0.090	0.028	0.3
Comp12_3	0.125	0.039	0.3
Comp12_4	0.094	0.027	0.3
Comp11_2	0.144	0.045	0.3
Comp16_4	0.079	0.027	0.3
Comp10_3	0.214	0.033	0.7
Comp12_2	0.178	0.029	0.6
Comp17_1	0.032	0.027	0.1
Comp11_3	0.058	0.045	0.1
Comp17_2	0.068	0.022	0.3
Comp11_4	0.144	0.038	0.4
Mean	0.110	0.033	0.3

Appendix VI: Experimental determined elastic and viscous parameters for 15 SWCNT/epoxy composites using a 4-element Burgers model and their harmonic mean values.

Sample No.	σ (MPa)	$E_1(10^2\text{MPa})$	$E_2(10^2\text{MPa})$	η_2 ($10^6\text{MPa}\cdot\text{s}$)	η_3 ($10^6\text{MPa}\cdot\text{s}$)
Comp15_2	23.56	21.84	110.94	31.79	345.28
Comp10_1	23.87	18.98	63.98	31.90	153.98
Comp13_2	25.40	19.67	80.52	13.70	84.66
Comp13_1	27.72	20.81	116.22	34.94	99.01
Comp10_4	29.05	23.41	194.29	25.16	83.00
Comp12_3	30.07	21.52	150.20	6.88	31.32
Comp12_4	30.62	22.07	142.78	5.39	27.22
Comp11_2	30.71	21.05	120.10	10.24	54.84
Comp16_4	30.72	21.01	106.21	3.00	21.33
Comp10_3	30.77	24.68	158.28	9.07	50.36
Comp12_2	31.57	20.87	201.48	3.29	14.03
Comp17_1	31.66	19.37	61.91	9.08	58.63
Comp11_3	31.67	20.95	79.98	5.95	35.59
Comp17_2	32.52	19.34	70.18	9.04	53.31
Comp11_4	33.38	22.44	210.87	4.31	19.79
Harmonic mean	29.55*	21.09	106.27	7.50	39.19

*Arithmetic mean.

Appendix VII: Experimental determined elastic and viscous parameters for 15 neat epoxy samples using a 4-element Burgers model and their harmonic mean values.

Sample No.	σ (MPa)	$E_1(10^2\text{MPa})$	$E_2(10^2\text{MPa})$	η_2 ($10^6\text{MPa}\cdot\text{s}$)	η_3 ($10^6\text{MPa}\cdot\text{s}$)
R2_3	25.13	24.22	127.57	6.87	23.59
R8_5	25.29	16.43	80.16	13.27	75.48
R5_1	28.49	20.17	115.29	17.28	93.39
R8_4	28.63	18.63	83.66	6.84	42.54
R5_3	28.68	19.78	152.01	10.87	51.22
R5_2	28.69	20.15	120.66	14.74	57.39
R5_4	29.63	19.29	85.35	4.02	32.20
R6_1	30.04	20.60	158.00	14.97	75.10
R6_2	31.61	18.98	128.24	9.66	44.51
R6_4	31.80	18.22	113.36	12.82	38.31
R4_4	32.86	18.83	168.96	3.12	13.12
R1_2	33.08	19.52	146.20	13.97	47.94
R6_5	33.23	21.43	163.46	5.23	22.92
R7_2	33.36	20.72	111.26	5.09	23.33
R7_1	33.60	20.71	136.20	4.55	15.27
Harmonic mean	30.27*	19.71	119.35	7.21	32.00

*Arithmetic mean