

A DAMAGE MECHANICS MODEL FOR TWISTED CARBON NANOTUBE FIBERS^{★★}

Qingqing Rong¹ Jianshan Wang^{1*} Yilan Kang¹ Yali Li² Qing-Hua Qin³

(¹Tianjin Key Laboratory of Modern Engineering Mechanics, Department of Mechanics, School of Mechanical Engineering, Tianjin University, Tianjin 300072, China)

(²Key Laboratory of Advanced Ceramics and Machining Technology, Ministry capable of Education, School of Materials Science and Engineering, Tianjin University, Tianjin 300072, China)

(³School of Engineering, Australian National University, Canberra, ACT 0200, Australia)

Received 16 November 2011, revision received 27 March 2012

ABSTRACT Carbon nanotube fibers can be fabricated by the chemical vapor deposition spinning process. They are promising for a wide range of applications such as the building blocks of high-performance composite materials and micro-electrochemical sensors. Mechanical twisting is an effective means of enhancing the mechanical properties of carbon nanotube fibers during fabrication or by post processing. However, the effects of twisting on the mechanical properties remain an unsolved issue. In this paper, we present a two-scale damage mechanics model to quantitatively investigate the effects of twisting on the mechanical properties of carbon nanotube fibers. The numerical results demonstrate that the developed damage mechanics model can effectively describe the elastic and the plastic-like behaviors of carbon nanotube fibers during the tension process. A definite range of twisting which can effectively enhance the mechanical properties of carbon nanotube fiber is given. The results can be used to guide the mechanical twisting of carbon nanotube fibers to improve their properties and help optimize the mechanical performance of carbon nanotube-based materials.

KEY WORDS carbon nanotube fibers, damage, twisting, multi-level structures, elastic modulus

I. INTRODUCTION

Carbon nanotube (CNT) fibers have been shown to possess impressive physical properties such as low density, high strength and modulus^[1], great thermal and electrical conductivity^[2–5], which make them promising to be used for high-performance composite materials, micro electrochemical sensors and artificial muscles etc. Some macro-tensile tests show that the tensile strengths of CNT fibers produced by using different synthesis routes^[1, 4, 6–10] range from 0.3 to 10 GPa, which are much higher than those of other commercial fibers but far below than those of carbon nanotubes (CNTs) (≈ 150 GPa)^[11]. Thus the mechanical properties of CNT fibers limit their further applications to a certain degree.

As an effective method, twisting is often used to improve the mechanical properties of fibers. In recent years, there have been extensive researches on the twisting effects on macroscopic CNT assemblies, such as CNT bundles^[12, 13], CNT ropes or yarns^[14–17]. By increasing the contact areas between CNTs and the

* Corresponding author. Email: wangjs@tju.edu.cn

★★ Support from the 973 Program of Most (Grant Nos. 2012CB937500 and 2010CB934700), the National Natural Science Foundation of China (under Grant Nos. 10732080 and 10802041), Key Grant of Chinese Ministry of Education (309010) is acknowledged.

density of CNT fibers, the interaction between CNTs becomes strong and the mechanical properties of these materials are distinctly improved. Many works revealed that the load transfer between neighboring tubes was significantly enhanced after twisting in a single walled carbon nanotube (SWCNT) bundle; some specific tensile properties of CNT yarns including strength, toughness, modulus and Poisson's ratio can be affected significantly by the twisting. Generally, the yarn's specific strength, toughness and specific modulus initially increased with an increase of the twisting angle, peaked at a certain twisting angle and then started to decrease as twisting became excessive. Liang and Upmanyu^[14] developed a hybrid atomistic-continuum model to investigate the effects of twisting on the size of the assembly of CNT ropes. For CNT yarns spun using downsizing ancient technology, the ratio of twisted fiber tensile strength (σ_f) to the tensile strength of the CNTs (σ_b) was predicted approximately as $\sigma_f/\sigma_b \approx \cos^2 \alpha (1 - k \csc \alpha)$, where α is the twisting angle, k is a coefficient related to CNT diameter, length, and friction between CNTs^[18]. In addition, Shi et al.^[19] investigated the effects of helical shape of CNTs on the elastic properties of CNT-reinforced composites using a micromechanics model developed. For most previously studied CNT fibers, they are usually simple twisting-induced assemblies of single or ultrawalled CNTs such as bundles or ropes rather than hierarchical structures and their damage during the loading process is generally not concerned. While for CNT fibers produced by the chemical vapor deposition spinning process^[20], they often have complicated multi-level structures which, in turn, induce complicated load transfer and damage evolution during the loading process. In this case, both the defects of CNTs and the debonding and/or sliding between CNTs or CNT bundles can be regarded as damage, which is crucial for the load transfer in CNT fibers. During the fabrication or subsequent process of such CNT fibers, mechanical twisting has been actively pursued as an effective means to tailor the mechanical properties of CNT fibers. Unfortunately, the physical mechanism underlying the twisting treatment of improving the mechanical properties of CNT fibers is still unclear owing to the complicated hierarchical structures.

Therefore, the purpose of this paper is to quantitatively investigate the mechanism of the twisting effects on the mechanical properties of CNT fibers. Considering the hierarchical structures of CNT fibers, we have developed a two-scale damage mechanics model on the basis of the traditional parallel bar model^[21] to investigate the effects of twisting on the elastic properties during the tension process from the damage mechanics point of view. It should be mentioned that, for such CNT fibers with hierarchical structures, the stochastic damage mechanical methods^[21] can also be used to study their mechanical behaviors.

II. DAMAGE MECHANICS MODEL FOR TENSION BEHAVIORS OF TWISTED CNT FIBERS

As shown in Fig.1(a), CNT fibers produced in the chemical vapor deposition spinning process have complicated multi-level structures, which can be classified into CNT bundles and amorphous CNT threads. The CNT bundles have consistent orientations and are usually arranged parallel, while the amorphous CNT threads, being much thinner than CNT bundles, fill between CNT bundles to form a certain network structure^[22]. The multi-level structures of twisted CNT fibers including the CNT bundles and the amorphous CNT threads, are shown in Figs.1(a)-(d). During the twisting process, the CNT fibers become thinner while the contact areas between CNTs are increased. However, when the twisting exceeds a certain extent, CNTs and CNT bundles in the fibers may slide and even fracture. For twisted CNT fibers, the twisting angle θ as shown in Fig.1(b)

is used to describe the extent of twisting. In this paper, the twisting angle θ of each CNT bundle is assumed to be constant for simplicity. For CNT fibers, tension tests are usually performed to measure

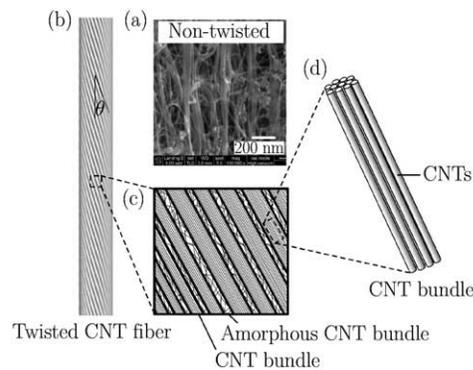


Fig. 1 The microscopic morphologies of CNT fiber (a) and the model schematic of twisted CNT fiber ((b)-(d)). (a) A Scanning Electron Microscope (SEM) image observed on the fiber surface^[22]. (b) Twisted CNT fiber with a certain twisting angle θ . (c) Complicated structures classified into CNT bundles and amorphous CNT threads. (d) CNTs in the CNT bundle have consistent orientation and are arranged parallel.

their mechanical properties and examine the effects of twisting. When the CNT fibers are tensioned, the CNT bundles mainly bear the loads, while the amorphous CNT threads act as imperfect interfaces between CNT bundles to bear the shear stresses. Then the load is transferred to the bundles and the CNTs in the fibers. With an increase of the load, the degree of the curling of the CNT threads will be reduced and can even become straight, enabling the threads to bear tension stresses instead of shear stresses. Furthermore, the fracture of CNTs and the debonding and sliding between CNTs or bundles occur and induce energy dissipation. Then the fiber will be enabled to bear an increasingly large load, which induces a plastic-like stress-strain relationship. During the loading process, the damage is initiated and continues to accumulate with the increase of the load, and apparent effects on the stress transfer in the fiber. In the following, we will develop a two-scale parallel bar model to describe such plastic-like behavior of the fiber and account for the effects of the twisting.

The twisted CNT fiber is assumed to consist of N CNT bundles with the twisting angle θ , where n CNT bundles have initiated damage. Furthermore, these N CNT bundles include M_i ($i = 1, 2, \dots, N$) CNTs respectively and in the n damaged CNT bundle there are m_i ($i = 1, 2, \dots, n$) damaged CNTs. We use k_f to denote the average stiffness of the twisted CNT fiber without damage, and it is a constant for a certain twisting angle θ . k'_f , a random variable, is used to denote the equivalent stiffness of the twisted CNT fiber in which some CNT bundles have been damaged. In addition, the length of the twisted CNT fiber is L . The internal force of the i th ($i = 1, 2, \dots, N$) CNT bundle, f_i , is composition of forces of M_i ($i = 1, 2, \dots, N$) CNTs consisted in the i th ($i = 1, 2, \dots, N$) CNT bundle. It should be noted that the forces in damaged CNTs and those in non-damaged CNTs are different. Thus, the internal force of the i th ($i = 1, 2, \dots, n$) damaged CNT bundle, f_i , is

$$f_i = \sum_{m_i+1}^{M_i} \frac{k_f}{M_1 + M_2 + \dots + M_N} z \cos \theta + \sum_1^{m_i} \frac{k'_f}{M_1 + M_2 + \dots + M_N} z \cos \theta \quad (1)$$

For the i th ($i = n + 1, n + 2, \dots, N$) non-damaged CNT bundle, we have

$$f_i = \sum_1^{M_i} \frac{k_f}{M_1 + M_2 + \dots + M_N} z \cos \theta \quad (2)$$

In Eqs.(1) and (2), z and $z \cos \theta$ are the extension of the twisted CNT fiber and the CNT bundle due to the active force F , respectively. $k_f/(M_1 + M_2 + \dots + M_N)$ and $k'_f/(M_1 + M_2 + \dots + M_N)$ are the average stiffness and equivalent stiffness of each CNT, respectively. The equilibrium of internal forces along the longitudinal direction of CNT bundle can be written as

$$F' = \sum_{i=1}^n \left(\sum_{m_i+1}^{M_i} \frac{k_f}{M_1 + M_2 + \dots + M_N} z \cos \theta + \sum_1^{m_i} \frac{k'_f}{M_1 + M_2 + \dots + M_N} z \cos \theta \right) + \sum_{i=n+1}^N \sum_1^{M_i} \frac{k_f}{M_1 + M_2 + \dots + M_N} z \cos \theta \quad (3)$$

where $F' = F \cos \theta$. Then by introducing $r_i = M_i/(M_1 + M_2 + \dots + M_N)$ ($i = 1, 2, \dots, N$) and $\omega_{ci} = m_i/M_i$ ($i = 1, 2, \dots, n$), we can obtain the expression of active force F ,

$$F = \sum_{i=n+1}^N k_f z r_i + \sum_{i=1}^n k_f z r_i (1 - \omega_{ci}) + \sum_{i=1}^n k'_f z r_i \omega_{ci} \quad (4)$$

The variables ω_{ci} ($i = 1, 2, \dots, n$) are the measurement of damage in the CNT bundles and r_i ($i = 1, 2, \dots, N$) are fraction factors of each of CNT bundles to the fiber. The continuum form of Eq.(4) can be readily recovered by setting $F = \sigma A_0$, $k_f = E_f A_0/L$, $k'_f = \beta_f k_f$, and $z = \varepsilon L$, in which σ is the axial component of the nominal stress and A_0 is the cross-sectional area of the twisted CNT fiber. The term ε is the axial component of the nominal strain, and β_f is the stiffness ratio which can be a random variable. Then,

$$\sigma = E_f \left[\left(1 - \sum_{i=1}^n r_i \omega_{ci} \right) + \beta_f \sum_{i=1}^n r_i \omega_{ci} \right] \cdot \varepsilon \quad (5)$$

As ω_{ci} ($i = 1, 2, \dots, n$) is the damage of individual CNT bundle, the damage of CNT fiber can then be expressed as $\omega_f = \sum_{i=1}^n r_i \omega_{ci}$. A clear implication can be seen from Eq.(5) that when $\omega_f = 0$, i.e., no damage is initiated, $\sigma = E_f \varepsilon$. That is, the twisted CNT fiber with a certain twisting angle behaves elastically. While $\omega_f = 1$, i.e., damage has occurred in all CNT bundles of the CNT fiber, $\sigma = E_f \beta_f \varepsilon$, where β_f is now equal to zero so that $\sigma = 0$. In other words, the twisted CNT fiber cannot bear any load. Consequently, a rationble stress-strain relationship is obtained by this model.

For simplicity, we consider the twisted fiber as an ideal structure. All CNT bundles have the same number of CNTs and all damaged bundles have the same number of damaged CNTs, i.e., $M_i = M$ ($i = 1, 2, \dots, N$) and $m_i = m$ ($i = 1, 2, \dots, n$). Thereby, Eq.(5) can be simplified to

$$\sigma = E_f \left[\left(1 - \frac{n}{N} \omega_c \right) + \beta_f \frac{n}{N} \omega_c \right] \cdot \varepsilon \quad (6)$$

where $\omega_c = m/M$, and n/N ranges from 0 to 1, while n and m are not constant in the tension process.

The Young's modulus E_f of twisted CNT fibers without damage in Eq.(6) initially increases with the increase of the twisting angle, then reaches a plateau and finally starts to decrease as the twisting becomes excessive^[16]. E_f can be viewed as a function of the twisting angle, i.e., $E_f(\theta)$, and it can be expanded into a Taylor series,

$$E_f(\theta) = \sum_{n=0}^{\infty} \frac{E_f^n(0)}{n!} \theta^n \quad (7)$$

When these undetermined coefficients E_f^n are determined, the function $E_f(\theta)$ can be obtained. Usually, the modulus of the CNT fiber can be expressed as a following quadratic function of the twisting angle,

$$E_f(\theta) = A(\theta - \theta_E)^2 + E_{f\max} \quad (8)$$

where θ_E is the twisting angle at which the modulus reaches the maximal value $E_{f\max}$, and A is a constant. When $\theta = 0$, it yields

$$E_f(0) = A\theta_E^2 + E_{f\max} \quad (9)$$

Thus, $A = (E_f(0) - E_{f\max})/\theta_E^2$. Then, the modulus function $E_f(\theta)$ can be rewritten as

$$E_f(\theta) = \frac{E_f(0) - E_{f\max}}{\theta_E^2} (\theta - \theta_E)^2 + E_{f\max} \quad (10)$$

In this paper, the damage variable ω_f can be phenomenologically defined as the decrease of the stiffness of the twisted CNT fiber. Based on the continuum damage model^[23], the damage variable ω_f can be written as

$$\omega_f = 1 - \frac{k'_f}{k_f} = 1 - \beta_f \quad (11)$$

From Eq.(11), we easily have

$$\beta_f = 1 - \omega_f = 1 - \frac{n}{N} \omega_c \quad (12)$$

For the tension process of the fiber, we assume the damage is only a following piecewise function of the axial strain component ε .

$$\omega_c = \begin{cases} 0 & (\varepsilon < \varepsilon_0) \\ \frac{\varepsilon - \varepsilon_0}{\varepsilon + (\varepsilon_1 - \varepsilon_0)/C} & (\varepsilon_0 \leq \varepsilon < \varepsilon_1) \\ 1 & (\varepsilon \geq \varepsilon_1) \end{cases} \quad (13)$$

in which ε is the axial strain component of twisted CNT fibers, and ε_1 is the critical axial strain component, i.e., the elongation of CNT fibers when the damage variable $\omega_c = 1$, and C is a constant. During the tension of the twisted CNT fiber^[24], the elongation of twisted CNT fibers usually varies with the twisting angle θ and can be given approximately as

$$\varepsilon_1 = y_0 + B \sin \left[\frac{\pi}{w} (\theta - \theta_c) \right] \quad (14)$$

The parameters of y_0 , B , w and θ_c can be determined using relevant experimental results.

III. RESULTS AND DISCUSSIONS

The stress-strain curves obtained from the constitutive model characterized by Eq.(6) show the tensile response of twisted CNT fibers under axial tension and can explain the mechanism of twisting effects on their tensile properties. The parameters of this model are related to those of the twisted CNT fibers of different lengths, cross-sectional areas, and synthetic patterns. The values of these parameters are found to be $E_f(0) = 12.7$ GPa, $E_{f\max} = 68.4$ GPa, $\varepsilon_0 = 1\%$, $\theta_E = 24.7^\circ$, $y_0 = 0.173$, $B = 0.0368$, $w = 0.1229$, $\theta_c = -0.027$ rad = -1.547° based on the experimental results^[24]. Additionally, C and n/N are given as 7 and 0.85, respectively. The stress-strain relationships can be obtained and are shown in Fig.2. The tension process of twisted CNT fibers is divided into three stages, i.e. the initial linear stage, the nonlinear stage induced by the evolution of damage, and the final failure of fibers. With an increase of the twisting angle, the tensile curves tend to rise and the fracture of the fibers may occur. In a definite range of twisting approximately below 28° , the larger the twisting angle is, the greater the tension stress is at the same strain level. But beyond the range the tensile stress will decline. Twisting makes the contact between CNTs closer and the Van der Waals and friction forces between CNTs larger. The tensile strength of CNT fibers is therefore improved. While over twisting which may make CNTs in fibers slip and even fracture, weakens the tensile strength. It shows a good agreement between the results in this paper and the experimental tensile curves^[24]. Thus, it is feasible to use the two-scale damage mechanics model to describe the tension behaviors of non-twisted or twisted CNT fibers. The parameters in the model can be further modified to study CNT fibers in other cases.

Figure 3 plots the variation of CNT fibers' Young's modulus E_f with the twisting angle θ . It demonstrates that the Young's modulus increases with an increase of the twisting angle until it reaches the highest value of about 25° , then the modulus begins to decline as the twisting angle continues to increase. The Young's modulus is related to CNT fibers' complicated structure and internal interaction which are affected by twisting as mentioned above. Figure 3 shows that the best twisting angle is about 25° at which the Young's modulus reaches the highest value. Although the twisting can improve the mechanical properties of CNT fiber, the excess twisting will destroy the structures of CNT fibers and then make the load-carrying capacity reduced.

IV. CONCLUSIONS

In this paper, a two-scale damage mechanics model is developed to investigate the mechanical properties of twisted CNT fibers. The stress-strain curves obtained from the model show the twisting treatment can enhance the mechanical properties of CNT fibers. It is pointed out that the optimized twisting angle range for best improving the CNT fiber under discussion is from 25° to 28° , which is consistent with previous experimental results^[24]. It is shown that the two-scale model developed can effectively describe the tensile behaviors of CNT fibers. Furthermore, the physical mechanism underlying the load transfer in the CNT fiber is also revealed. This study not only shows how the twisting improves the mechanical properties of the CNT fiber, but also is helpful to the design of CNT-based fiber materials.

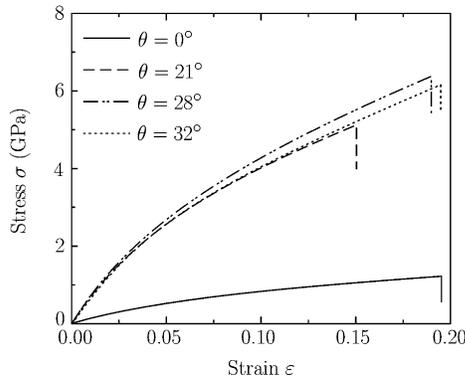


Fig. 2. Stress-strain curves of CNT fibers for different twisting angles.

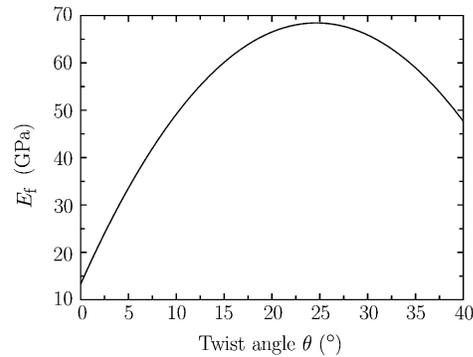


Fig. 3. Variation of elastic modulus E_f with the twisting angle θ .

References

- [1] Koziol,K., Vilatela,J., Moisala,A., Motta,M., Cunniff,P., Sennett,M. and Windle,A., High-performance carbon nanotube fiber. *Science*, 2007, 318(5858): 1892-1895.
- [2] Hone,J., Whitney,M., Piskoti,C. and Zettl,A., Thermal conductivity of single-walled carbon nanotubes. *Synthetic Metals*, 1999, 103(1-3): 2498-2499.
- [3] Berber,S., Kwon,Y.K. and Tomanek,D., Unusually high thermal conductivity of carbon nanotubes. *Physical Review Letters*, 2000, 84(20): 4613-4616.
- [4] Zhang,X.F., Li,Q.W., Tu,Y., Li,Y.A., Coulter,J.Y., Zheng, L.X., Zhao,Y.H., Jia,Q.X., Peterson,D.E. and Zhu,Y.T., Strong carbon-nanotube fibers spun from long carbon-nanotube arrays. *Small*, 2007, 3(2): 244-248.
- [5] Li,Q.W., Li,Y., Zhang,X.F., Chikkannanavar,S.B., Zhao,Y.H., Dangelewicz,A.M., Zheng,L.X., Doorn,S.K., Jia,Q.X., Peterson,D.E., Arendt,P.N. and Zhu,Y.T., Structure-dependent electrical properties of carbon nanotube fibers. *Advanced Materials*, 2007, 19(20): 3358-3363.
- [6] Vigolo,B., Penicaud,A., Coulon,C., Sauder,C., Pailler,R., Journet,C., Bernier,P. and Poulin,P., Macroscopic fibers and ribbons of oriented carbon nanotubes. *Science*, 2000, 290(5495): 1331-1334.
- [7] Vigolo,B., Poulin,P., Lucas,M., Launois,P. and Bernier,P., Improved structure and properties of single-wall carbon nanotube spun fibers. *Applied Physics Letters*, 2002, 81(7): 1210-1212.
- [8] Jiang,K.L., Li,Q.Q. and Fan,S.S., Nanotechnology: Spinning continuous carbon nanotube yarns—Carbon nanotubes weave their way into a range of imaginative macroscopic applications. *Nature*, 2002, 419(6909): 801-801.
- [9] Zhu,H.W., Xu,C.L., Wu,D.H., Wei,B.Q., Vajtai,R. and Ajayan,P.M., Direct synthesis of long single-walled carbon nanotube strands. *Science*, 2002, 296(5569): 884-886.
- [10] Li,Y.L., Kinloch,I.A. and Windle,A.H., Direct spinning of carbon nanotube fibers from chemical vapor deposition synthesis. *Science*, 2004, 304(5668): 276-278.
- [11] Demczyk,B.G., Wang,Y.M., Cumings,J., Hetman,M., Han,W., Zettl,A. and Ritchie,R.O., Direct mechanical measurement of the tensile strength and elastic modulus of multiwalled carbon nanotubes. *Materials Science and Engineering a—Structural Materials Properties Microstructure and Processing*, 2002, 334(1-2): 173-178.
- [12] Liew,K.M., Wong,C.H., Tan,M.J. and Chuang,P.D., Non-twisted and twisted CNT bundles under axial tensile and compressive loads. *Nanoscience and Technology*, Pts 1 and 2, 2007, 121-123: 1415-1418.
- [13] Qian,D., Liu,W.K. and Ruoff,R.S., Load transfer mechanism in carbon nanotube ropes. *Composites Science and Technology*, 2003, 63(11): 1561-1569.
- [14] Liang,H.Y. and Upmanyu,M., Size dependent intrinsic bulk twisting of carbon nanotube ropes. *Carbon*, 2005, 43(15): 3189-3194.
- [15] Fang,S.L., Zhang,M., Zakhidov,A.A. and Baughman,R.H., Structure and process-dependent properties of solid-state spun carbon nanotube yarns. *Journal of Physics-Condensed Matter*, 2010, 22(33), 334221.
- [16] Miao,M.H., McDonnell,J., Vuckovic,L. and Hawkins,S.C., Poisson's ratio and porosity of carbon nanotube dry-spun yarns. *Carbon*, 2010, 48(10): 2802-2811.
- [17] Sears,K., Skourtis,C., Atkinson,K., Finn,N. and Humphries,W., Focused ion beam milling of carbon nanotube yarns to study the relationship between structure and strength. *Carbon*, 2010, 48(15): 4450-4456.
- [18] Zhang,M., Atkinson,K.R. and Baughman,R.H., Multifunctional carbon nanotube yarns by downsizing an ancient technology. *Science*, 2004, 306(5700): 1358-1361.
- [19] Shi,D.L., Feng,X.Q., Huang,Y.Y., Hwang,K.C. and Gao,H., The effect of nanotube waviness and agglomeration on the elastic property of carbon nanotube-reinforced composites. *Journal of Engineering Materials and Technology*, 2004, 126(3): 250-257.
- [20] Zhong,X.H., Li,Y.L., Liu,Y.K., Qiao,X.H., Feng,Y., Liang,J., Jin,J., Zhu,L., Hou,F. and Li,J.Y., Continuous multilayered carbon nanotube yarns. *Advanced Materials*, 2010, 22(6): 692-696.
- [21] Li,F.M. and Li,Z.J., Continuum damage mechanics based modeling of fiber reinforced concrete in tension. *International Journal of Solids and Structures*, 2001, 38(5): 777-793.
- [22] Li,Q., Kang,Y.L., Qiu,W., Li,Y.L., Huang,G.Y., Guo,J.G., Deng,W.L. and Zhong,X.H., Deformation mechanics of carbon nanotube fibers under tensile loading by in situ Raman spectroscopy analysis. *Nanotechnology*, 2011, 22, 225704.
- [23] Krajcinovic,D., *Damage Mechanics*. Netherlands: Elsevier Science B.V., 1996.
- [24] Liu,Y.K., *Structures and Mechanical Properties of Carbon Nanotube Yarns by Mechanical Processing and Composite*. M.S. Dissertation, Tianjin University, 2009, 33-42 (in Chinese).