A MULTI-SCALE EXPERIMENTAL ANALYSIS FOR MECHANICAL PROPERTIES OF CARBON NANOTUBE FIBERS BY RAMAN SPECTROSCOPY

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Abstract

In this work, The mechanical properties of CNT fibers spun from CVD aerogel are tested by tensile experiment and in-situ Raman spectroscopy. It is found that , the G' band in the Raman spectrum responds distinctly to the tensile strain in Raman shift, width and intensity. The Raman shift changes with the tensile deformation of the fiber at different stages, namely elastic deformation, strengthening and damage-fracture. Based on the experimental results obtained, a physical model for the load-bearing and deformation of micro-structures in fibers and a constitutive equation are developed to explain and describe the tensile mechanical properties of CNT fiber materials.

1 Introduction

Due to the high specific stiffness, high specific strength and other outstanding mechanical properties, carbon nanotubes (CNTs) have been widely expected as ideal building blocks for high performance engineering materials. CNT structures with macro-scale, such as CNT film [1] and CNT fiber [2], have been prepared and developed successively. However, it is still a challenge to prepare macro CNT materials with super mechanical properties. Recent works have demonstrated that the mechanical properties of many CNT fibers are far away from those of the typical single-walled CNTs (e.g., 640Gpa modulus and 37Gpa strength [3]). For example, CNT fibers spun directly from the liquid crystalline suspension of single-walled CNTs by Ericson etc, have the modulus of 120Gpa and the strength of 0.1Gpa only [4]. For the CNT fibers spun from the arrays of multi-walled CNTs, the modulus is 330 GPa and the strength 1.9 GPa [5]. While for the continuous CNT fibers spun directly from an aerogel of CNTs as they are formed in a chemical vapor deposition (CVD) reactor, the modulus is 350Gpa and the strength 9Gpa [6]–[9]. Moreover, it has been shown that, the mechanical properties of CNT fibers prepared from different methods can vary greatly. To understand the much difference and change, and improve the mechanical performance of CNT-based materials, the mechanical properties and their underlying control mechanisms need to be known.

In this work, the tensile mechanical properties of CNT fibers have been investigated by multi-scale experiment. The outline of this paper is as follows. Firstly, the macroscopic tension experiments and in-situ micro-Raman tests on CNT fibers are carried out. Based on the experimental results, the multi-scale deformation processes of continuous CNT fibers are analyzed. Then a micro-mechanical model and its mathematical expression is developed to describe the mechanical property of fibers. Finally, possible ways to improve the mechanical performance of CNT fiber materials are further discussed.

2 Experiment and Result

The continuous CNT fiber materials used for measurement are spun directly from CNT aerogel formed by CVD process [10]. The fibers have a diameter of 100–150μm. Their micro morphologies are shown in the illustration in Fig. 1. It could be seen that, fibers are composed of countless CNT congeries, which are mainly in two forms: straight and bending. The thick & straight ones are named nanotube bundles, while the fine & bending ones are named nanotube threads. The nanotube bundles are arranged nearly in parallel, and the nanotube threads join each other and fill in among the nanotube bundles.

The uniaxial tension of the fibers was performed by precise micro-loading device [11]. The spectroscopic data during the uniaxial tension were collected in situ by a Renishaw InVia Raman spectroscope in back scattering configuration under a 632.8 nm He-Ne laser incident light with polarization direction parallel to the fiber axial. The laser is focused on the fiber under objective of 50× with a spot of 2 μm in diameter.

Fig. 1 shows the stress-strain curve during the tensile process of the fiber until fracture. The deformation of the fiber can be divided into three stages, namely the elastic stage ($\varepsilon < 1\%$), the strengthening stage ($1\% < \varepsilon < 11.5\%$) and the damage-fracture stage ($\varepsilon > 11.5\%$).

The G' bands and their positions of the fiber under different loads are given in Fig. 2. It can be seen in the figure that, during the elastic stage the G' bands shift towards lower wavenumbers linearly with strain. This indicates that most CNTs have been loaded. During the strengthening stage, Raman shift of G' bands varies only a little with scatter, which indicates that the individual CNTs themselves deform only a little more than in the elastic stage. We attribute it to the slippage among CNTs. The broadening of the G' band means that distribution of load on the CNTs is non-uniform. And almost all broadening comes from the low-wavenumber edge. The asymmetric broadening of the G' band suggests that some of the CNTs even do not bear any load. Another change of the G' band under loads is that the intensity increases. This implies that the CNTs tend to align with the loading direction during deformation.

3 Discussion

Based on the multi-scale experimental results and microstructure characteristics of CNT fiber materials, a tensile micro-deformation process of the fibers is proposed, as shown in Fig. 3. During the elastic stage, under the action of tension force, the straight nanotube bundles bear the loads first, and their stresses increase linearly with the applied strain. Meanwhile, the nanotube threads are stretched gradually and become to bear small amount of loads, their stresses also increase with the applied strain. During the strengthening stage, the stresses of nanotube bundles exceed the interface shear limits among the CNTs, which led to the slips among CNTs and great deformations of the nanotube bundles. Meanwhile, lots of the nanotube threads are gradually straightened up to bear more loads. During damage-fracture stage, although part of the nanotube threads are still bearing loads, most bundles slip among carbon tubes until breaking away from each other or the nanotubes fracture at the defects. The continuous slipping among nanotube bundles and fracture at defect points will lead to the fracture of the fibers eventually.

Based on the above deformation process of CNT fiber materials, a mechanical model will be developed in the following. As shown in Fig. 3, nanotube bundles and threads are considered as two parts of load-bearing materials denoted as Material 1 and Material 2 respectively. The fiber can be taken as a quasi-one dimensional material and it should satisfy the equilibrium and deformation compatibility conditions:

$$d\varepsilon = d\varepsilon_1 = d\varepsilon_2, \tag{1}$$

$$d\sigma = V_1 d\sigma_1 + V_2 d\sigma_2, \tag{2}$$

where $d\varepsilon$ and $d\sigma$ are the effective strain increment and the effective stress increment respectively of the fiber, $d\sigma_1$, $d\sigma_2$, $d\varepsilon_1$ and $d\varepsilon_2$ are the average stress and average strain increments of Material 1 and Material 2 respectively, V_1 ($0 \le V_1 \le 1$) and $V_2 (=1-V_1)$ represented the volumetric fractions of Material 1 and Material 2 respectively.

When the stress of nanotube bundles reaches the interface shear limits among the CNTs, the nanotube bundles might yield as a result of slippage among CNTs. Therefore, stress-strain relation of Material 1 are described by the Ramberg-Osgood (RO) model [12]:

$$\frac{\varepsilon_1}{\varepsilon_0} = \frac{\sigma_1}{\sigma_0} + C\left(\frac{\sigma_1}{\sigma_0}\right)^n, \tag{3}$$

Where σ_0, $\varepsilon_0 = \sigma_0 / E_1$ are the yield stress and yield strain of Material 1 respectively, E_1 is the Young's modulus of Material 1, C and n (n >1) are the strengthening coefficient and strengthening index of Material 1 respectively.

According to deformation characteristics of the nanotube threads, Material 2 could be regarded as a linear elastic material, and its stress-strain relation could be written as

$$\sigma_2 = E_2 \varepsilon_2, \tag{4}$$

where E_2 is the Young's modulus of Material 2, and $E_2 \ll E_1$.

From Eqs. (1) – (4), the constitutive equation of tensile deformation of CNT fibers can be obtained as

$$\frac{\varepsilon}{\varepsilon_0} = \frac{1}{V_1}\left(\frac{\sigma}{\sigma_0} - \frac{V_2 E_2 \varepsilon}{E_1 \varepsilon_0}\right) + \frac{C}{V_1^n}\left(\frac{\sigma}{\sigma_0} - \frac{V_2 E_2 \varepsilon}{E_1 \varepsilon_0}\right)^n. \tag{5}$$

From our SEM measurements, we estimated the approximate volume fraction of the bundles in the fibers V_1 is 80%. E_2/E_1 is taken as 0.01. By least square fitting the experiment data shown in Fig. 1 with Eq. (5), the strengthening coefficient C and strengthening index n are obtained to be 0.02 and 8 respectively. The fitted curve is shown in Fig. 4. Then, we achieve the constitutive relation for CNT fiber as follows:

$$\frac{\varepsilon}{\varepsilon_0} = 1.247 \cdot \frac{\sigma}{\sigma_0} + 0.119\left(\frac{\sigma}{\sigma_0} - 0.002 \cdot \frac{\varepsilon}{\varepsilon_0}\right)^8. \tag{6}$$

We can employ Eq. (6) to describe the mechanical property of the fibers.

4 Conclusion

Overall, the mechanical properties of CNT fiber materials has been investigated by macroscopic tension experiment and in-situ micro-Raman test at multi-scale levels. The tension and in-situ micro-Raman tests on CNT fibers show that, the G' band in the Raman spectrum responds distinctly to the tensile strain in Raman shift, width and intensity. The Raman shift changes with the tensile deformation of the fiber at different stages, namely elastic deformation, strengthening and damage-fracture. This work shows the mechanical properties of CNT fibers are strongly dependent on the micro-structures. Under the tensile loading, deformation of fibers mainly includes three distinct stages namely elastic stage, strengthening stage and damage-fracture stage. The loads are mainly borne by nanotube bundles in the elastic stage, so more nanotube bundles would result in greater fiber modulus. The deformation of fibers in the strengthening stage is caused by slippage among CNT in nanotube bundles and the gradual straightening of nanotube threads. Therefore, to make full use of the superior mechanical properties of CNTs in fibers, efforts may be worthwhile to enhance shear strength of interfaces among CNTs.

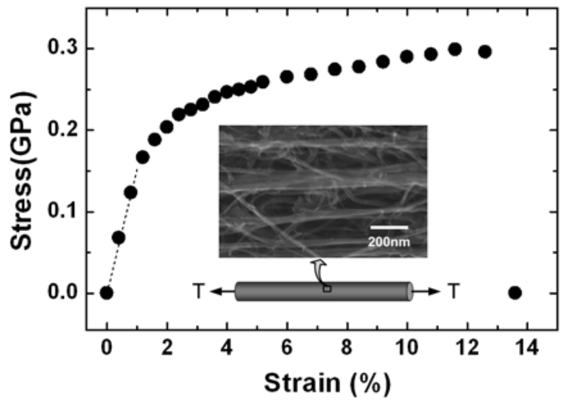

Fig.1. The change of the stress of the CNT fiber with the strain ε. The inset is uniaxial tension schematic illustration of the fiber and SEM image of it.

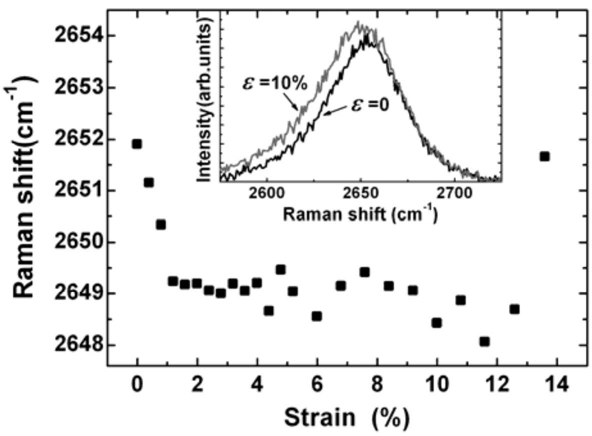

Fig.2. The change of G' band position with the strain. The inset shows G' bands under typical load conditions.

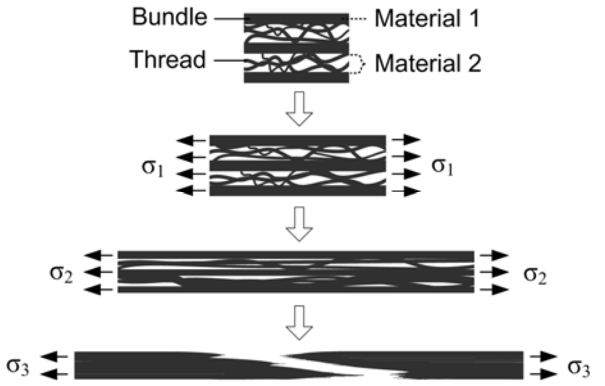

Fig.3. Load-bearing and deformation of micro-structures in CNT fibers under tensile loading. σ_1, σ_2 and σ_3 are the uniform loads.

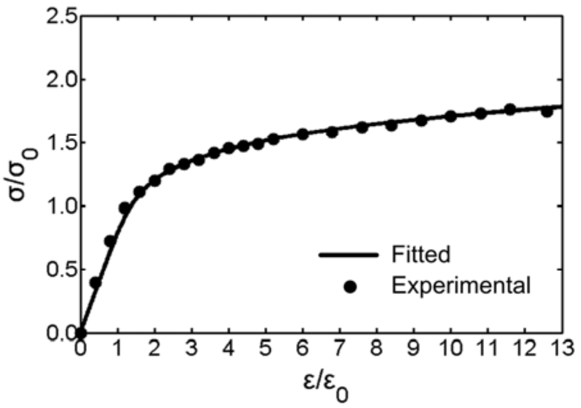

Fig.4. Fitted strain-stress curve (solid line) for the CNT fiber.

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