Static and dynamic mechanical properties of impregnated carbon nanotube fiber

Shan-Xiu Wan, Qing-Sheng Yang

Department of Engineering Mechanics, Beijing University of Technology, Beijing 100124, China

Corresponding author, Tel./Fax: +86-10-67396333, E-mail: qsyang@bjut.edu.cn

Abstract. Carbon nanotube fiber (CNT fiber) with excellent electrical and mechanical properties, as well as stable thermal and chemical properties has great potential application in areas such as ultra-fine wires, ultra-light cables, sensors, composite materials, energy conversion and electro-actuation. In this paper, the static and dynamic mechanical properties of impregnated CNT fiber were studied through single and cyclic tensile experiments and continuous dynamic analysis (CDA). The dynamic properties of impregnated CNT fiber such as storage and loss modulus was obtained. In addition, the storage modulus and loss modulus of impregnated CNT fiber increases with the increase of loading frequency. The research work in this paper has an important reference value for the engineering applications of impregnated CNT fiber in the fields of sensors and composites.

Keywords: Impregnated CNT fiber; Continuous dynamic analysis (CDA); Static elastic modulus; Storage modulus; Loss modulus

1. Introduction

Carbon nanotube (CNT) have excellent electrical and mechanical properties as well as stable thermal and chemical properties [1], thus they have been widely concerned by many scientists in the fields of physics, chemistry, materials and electronics. The results of theoretical prediction and experimental measurement [2-6] show that the mechanical properties of CNT exceed those of ordinary fiber materials, with young’s modulus reaching 1 TPa, tensile strength higher than 100 GPa, and elongation at break as high as 15%-30%. At the same time, CNTs have good flexural recoverable properties [7,8], which can be completely restored to the initial state after stress relief [9]. By assembling CNTs, CNT fiber with macroscopic one-dimensional structure can be obtained. CNT fiber, as a new material, has unique assembly structure characteristics and great application potential in energy, electronics, drive and other fields. As a new reinforcing material, the CNT fiber treated by epoxy resin impregnation has been widely used in aerospace, bulletproof equipment, sports equipment and other fields [10-12], while its interfacial properties have attracted much attention. Zu [13] used the droplet debonding test method to obtain an interfacial shear strength of about 14.4 MPa between CNT fiber/epoxy resin. Deng [14] applied the monofilament crack test method to obtain the interfacial shear strength between CNT fiber/epoxy resin, which ranged from 12 to 20 MPa. However, the current research only deals with the interfacial shear properties of CNT fiber/epoxy resin, there are few reports on the static and dynamic mechanical properties of carbon-impregnated CNT fiber. Therefore, it is of great significance to study the static and dynamic mechanical properties of impregnated (epoxy resin) CNT fiber. This paper based on UTM T150 stretching experiment system built stretching experiment platform, and the mechanical parameters of the impregnated CNT fiber under static and dynamic forces were obtained by single-stretching and
cyclic-stretching experiments. Meanwhile, the experimental results and microstructures of the impregnated/unimpregnated CNT fiber were compared and analysed.

2. Experimental methods and materials

2.1. Materials
In this experiment, the CNT fiber (SCNC-F800) was prepared by dry spinning with array method, and the fiber parameters were as follows: diameter 5-12 μm, strength 800-1000 MPa, modulus 50-100 GPa, tensile rate 2-3.5%, density 0.3-0.5 g/cm³, electrical conductivity $5 \times 10^4-7 \times 10^4$ S/m (Figure 1). The epoxy resin solution is composed of epoxy resin E51 and curing agent D400.

2.2. Experimental instrument
The tensile instrument used in this experiment is UTM T150 micro-nano tensile test system (as shown in Figure 2 and Figure 3) manufactured by Agilent company in the United States, which is suitable for the characterization of micro-nano mechanical properties of a variety of materials. The nanomechanical excitation sensor along with capacitance displacement sensor can be used to accurately test and analyse the static and dynamic micro tensile properties of samples within the design range ($50\mu N < \text{dynamic load range} < 500mN$).

2.3. Single tensile test

Figure 1. Carbon nanotube fiber (SCNC-F800)

Figure 2. Core components of micro-nano tensile system

Figure 3. UTM T150 micro-nano tensile system
The UTM T150 tensile test system was used to conduct a single tensile test on CNT fiber. We mixed E51 epoxy resin and curing agent D400 according to the ratio of 5 to 1 and infiltrated the CNT fiber in the configured epoxy resin solution. Then, the CNT fiber was taken out after fully infiltrates and placed within 100°C oven curing 1 hour. The CNT fiber were covered along the center of the window frame cardboard and fixed with epoxy glue at both ends. The central hole opening distance of window shaped cardboard is 10mm and the prepared sample was cured in an oven at 60°C for 2 hours. After the tensile specimen was obtained, the tensile test was performed with the UTM T150 tensile test system.

2.4. **Cyclic tensile test**

The prepared impregnated/unimpregnated CNT fiber tensile samples were placed on the UTM T150 tensile test system. The loading cycles were set to 20 times and the maximum strain values were set to be different. Finally, the changes of residual strain of impregnated/unimpregnated CNT fiber were observed.

3. **Single tensile test results**

It can be seen from the Figure 4 that the diameter of the CNT fiber has a certain degree of fluctuation along the longitudinal direction of the fiber. Accordingly, the diameter of CNT fiber have a certain degree of unevenness. Figure 5 shows the SEM image of the impregnated CNT fiber, which is coated with a thin layer of epoxy resin.

![Figure 4](image1.png)
**Figure 4.** Surface SEM image of unimpregnated CNT fiber

![Figure 5](image2.png)
**Figure 5.** Surface SEM image of unimpregnated CNT fiber

![Figure 6](image3.png)
**Figure 6.** Cross-sectional SEM photograph of unimpregnated CNT fiber

![Figure 7](image4.png)
**Figure 7.** Cross-sectional SEM photograph of impregnated CNT fiber

Figure 6 and Figure 7 respectively show the SEM photos of the unimpregnated/impregnated CNT fiber. It can be seen that a large amount of epoxy resin is soaked in the fiber and adhered to the CNT bundles and filaments.
Figure 8 shows the stress-strain curves of impregnated/unimpregnated CNT fiber in a single tensile process. It is found that the two kinds of fibers present three stages in the process of static force stretching: elastic stage, yield stage and fracture stage. The fracture strain values are almost the same whereas the fracture stress of the impregnated CNT fiber are significantly higher than unimpregnated CNT fiber, and the fracture stress increases by nearly 300 Mpa. This is mainly because there are many pores inside the CNT fiber. After being impregnated with epoxy resin [15], the resin molecules penetrate into the fibers through the pores inside the fibers to form a composite phase of a certain thickness, as a result the CNT fiber and the epoxy resin is well bonded to enhance the tensile strength of the CNT fiber.

Figure 9 and Figure 10 show the storage module-strain curves and loss module-strain curves of the impregnated/unimpregnated CNT fiber under the dynamic forces. It can be seen from the figure that the storage modulus and loss modulus of the impregnated/unimpregnated CNT fiber have similar change trends. Their storage modulus increase with the continuous increase of the dynamic force, while the loss modulus gradually tends to be stable. As can be seen from Figure 9, the storage modulus increase faster in the initial stage of dynamic force loading. With the continuous increase of dynamic force, although the storage modulus also increases, the increase speed decreases continuously. As shown in Figure 10, the loss modulus of the fiber increases rapidly to the peak in the initial stage of dynamic force loading. Then, with the continuous increase of dynamic force, the loss modulus first decreases and then gradually stabilizes. By observing the figure, the storage modulus and loss modulus of impregnated CNT fiber are significantly increased. The storage modulus is a parameter about the elasticity of the material, and the loss modulus is a parameter about the viscosity of the material. Accordingly, the elastic properties and viscous properties of impregnated CNT fiber are improved.
In order to clearly analyse the viscoelastic changes of CNT fiber after epoxy resin lipid immersion, we introduce the loss factor, whose formula is shown as follows:

\[
\tan\delta = \frac{E''}{E'}
\]

where \(\tan\delta\) represents the loss factor, \(E''\) represents the loss modulus, \(E'\) represents the storage modulus.

As can be seen from Figure 11, the strain of impregnated/unimpregnated CNT fiber increase continuously with the continuous loading of dynamic force, and the loss factor decreases gradually with the continuous increase of the strain. The size of the loss factor represents the viscoelastic properties of the material, the larger the loss factor, the greater the viscosity of the material and the smaller the loss factor, the greater the elasticity of the material. The loss factor of CNT fiber decreases obviously after immersion, which indicate that the influence of epoxy resin on the elastic property of CNT fiber was higher than that of the viscous property.
Figure 12 and Figure 13 are the tensile test results of impregnated CNT fiber at different loading frequencies. As can be seen from Figure 12 and Figure 13, the storage and loss modulus of impregnated CNT fiber increases significantly with the increase of loading frequency, but the loading frequency has no obvious effect on fracture strain.

4. Cyclic tensile test results
In order to analyse the residual strain of CNT fiber during stretching, we conducted a cyclic stretching experiment of impregnated/unimpregnated CNT fiber based on UTM T150 tensile system. Figure 14 and Figure 15 are unimpregnated CNT fiber stress-strain curves under cyclic loading at different strain. It can be seen that, the initial residual strain of CNT fiber is 0.345% when the maximum strain of 1% is set, while the initial residual strain of CNT fiber is 0.383% with the maximum strain of 1.25%. Moreover, residual strain of the CNT fibers increases with the increase of maximum strain. It can be seen from the results of the cyclic tensile test that as the number of cycle increases, the stress required for the CNT fiber to reach the maximum strain value is decreasing. At the same time, the residual strain of CNT fiber is also increasing. The reason is that there are many fiber bundles and filaments inside the CNT fiber, and the fiber bundles and filaments is gradually straighten due to external forces in the initial stages of cyclic loading. Meanwhile, the slip is occurred among the part of fiber bundles and filaments. The part of the slip is not restorable after unloading, and slip phenomenon is more obvious with the increase of cyclic number. As a result, the residual strain of CNT fiber becomes larger and the stress required to reach the maximum strain becomes smaller with the increase of loading times.
Figure 14. Stress-strain curve of CNT fiber (strain 1%)  

Figure 15. Stress-strain curve of CNT fiber (strain 1.25%)

Figure 16 and Figure 17 are stress-strain curves under cyclic loading of impregnated CNT fiber at different strain. It can be seen that, the initial residual strain of CNT fiber is 0.323% when the maximum strain of 1% is set, while the initial residual strain of CNT fiber is 0.375% with the maximum strain of 1.25%. Similar to the performance of unimpregnated CNT fiber, residual strain of the impregnated CNT fiber increases with the increase of maximum strain and the stress required for the CNT fiber to reach the maximum strain value is decreasing. The residual strain value of the impregnated CNT fiber increased more than unimpregnated CNT fiber after 20 cycles of loading due to the infiltration of epoxy resin.

Figure 16 shows the stress-strain curve of CNT fiber. It can be seen from the figure that the stress-strain curve mainly shows two modulus stages before reaching the yield stage. Mainly because the CNT fiber is composed of a large number of CNT fiber bundles, in which the carbon nanotube fiber bundles are connected by van der Waals force. On the one hand, the bent CNT fiber bundle is straightened due to the tensile effect. On the other hand [16], there is a relative slip among the bundles of carbon nanotubes that are not in the direction of stretching, and the bundles of carbon nanotubes gradually align towards the stretching direction, which corresponds to the first stage with the modulus of 46 GPa. When the slip reaches a certain degree, most of the CNT bundles undergo tensile stress and deform, and finally break, which corresponds to the second modulus of 60 GPa. Therefore, the slope of the stress-strain curve of the CNT fiber after the unloaded is larger than that of the CNT fiber at the initial loading.
5. Conclusions
This paper based on UTM T150 stretching experiment system built stretching experiment platform, and the mechanical parameters of the impregnated CNT fiber under static and dynamic forces were obtained by single-stretching and cyclic-stretching experiments. Meanwhile, the experimental results and microstructures of the impregnated/unimpregnated CNT fiber were compared and analysed, and draw the following conclusions:

(1) Compared with unimpregnated CNT fiber, the CNT fiber treated by epoxy resin infiltration has a significant improvement in tensile strength at break, which is increased by nearly 300 MPa. This mainly because the epoxy resin solution penetrates into the internal gap of the CNT fiber, and there is a good interaction between the two, thereby the strength of the CNT fiber is enhanced.

(2) As loading force continues to increase, the storage modulus of the impregnated/unimpregnated CNT fiber is also increased, and the loss modulus is gradually becoming stable. Compared with unimpregnated CNT fiber, the storage modulus and loss modulus of impregnated CNT fiber are significantly increased whereas the loss factor is smaller, which indicated that the influence of epoxy resin on the elastic properties of CNT fiber is higher than the viscous properties of that.

(3) With the increase of loading frequency, the storage modulus and loss modulus of impregnated CNT fiber increase significantly.

(4) The residual strain value of the impregnated/unimpregnated CNT fiber increases with the maximum strain increases. This is mainly because there are many fiber bundles and filaments inside the CNT fiber. The fiber bundles and filaments inside the fibers are gradually straightened due to the external force in the initial stage of cyclic loading. At the same time, some fiber bundles and filaments will slip between each other. The partial slip will not return to the original state when the force is unloaded, and the residual strain becomes bigger as the number of cycles increases.

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References
[1] Zhang X, Li Q, Holesinger T G, et al. 2010 Ultrastrong, stiff, and lightweight Carbon-nanotube fibers. *Adv Mater*. **19**(23): 4198-4201.

[2] Ghemes A, Minami Y, Muramatsu J, et al. 2012 Fabrication and mechanical properties of carbon nanotube yarns spun from ultra-long multi-walled carbon nanotube arrays. *Carbon*. **50**(12): 4579-4587.

[3] Deng W L, Qiu W, Li Q, et al. 2014 Multi-scale experiments and interfacial mechanical modeling of carbon nanotube fiber. *Exp Mech*. **54**(1): 3-10.

[4] Obaid A A, Heider D, Jr J W G. 2015 Investigation of electro-mechanical behavior of carbon nanotube yarns during tensile loading. *Carbon*. **93**: 731-741.

[5] Yang Z J, Yang Q S, Liu X, et al. 2015 Detailed investigation on elastoplastic deformation and failure of carbon nanotube fibers by monotonic and cyclic tensile experiments. *Carbon*. **94**: 73-78.

[6] Kalashnyk N, Faulques E, Schjodt-Thomsen J, et al. 2016 Strain sensing in single carbon fiber epoxy composites by simultaneous in-situ raman and piezoresistance measurements. *Carbon*. **109**: 124-130.

[7] Wang H, Cheng C, Zhang L, et al. 2014 Inkjet printing short-channel polymer transistors with high-performance and ultrahigh photoresponsivity. *Adv Mater*. **26**: 4683–4689

[8] Liu F Q, Liu X, Yang Q S. 2018 Experimental Research on electro-mechanical coupling effects of carbon nanotubes fibers. *J Mater Eng*. 1001-4381

[9] Reese C, Chung W J, Ling M M, et al. 2006 High-performance microscale single-crystal transistors by lithography on an elastomer dielectric. *Appl Phys Lett*. **89**: 202108

[10] Mora R J, Vilatela J J, Windle A H, et al. 2009 Properties of composites of carbon nanotube fibers. *Compos Sci Tech*. **69**(10): 1558-1563.

[11] Gao Y, Li J Z, Liu L Q, et al. 2010 Axial compression of hierarchically structured carbon nanotube fiber embedded in epoxy. *Adv Funct Mater*. **20**(21): 3797-3803.

[12] Pham G T, Park Y B, Kramer L, et al. 2008 Mechanical and electrical properties of polycarbonanotube buckypaper composite sheets. *Nanotechnology*. **19**(32): 325705.

[13] Zu M, Li Q w, Zhu Y, et al. 2012 The effective interfacial shear strength of carbon nanotube fibers in an epoxy matrix characterized by a microdroplet test. *Carbon*. **50**(3): 1271-1279.

[14] Deng F, Lu W, Zhao H, et al. 2011 The properties of dry-spun carbon nanotube fibers and their interfacial shear strength in an epoxy composite. *Carbon*. **49**(5): 1752-1757.

[15] Ren Yunhui, Li Hongfu, Zhang Boming. 2013 The interfacial load transfer efficiency testing and analyzing of the carbon nanotube fiber/epoxy resin composite. *Acta Mater Compos Sin*. **30**: 6443-01

[16] Ren Yunhui, Zhang Boming. 2014 Interfacial shear strength and microstructure of carbon nanotube fiber/epoxy composites. *Acta Mater Compos Sin*. **31**(5): 1206-06