Failure Mechanism and Property Improvement of Carbon-Nanotube Fibers

Yani Zhang,[a] Lianxi Zheng,[a]* Gengzhi Sun,[a] Zhaoyao Zhan,[a], Kin Liao[b]

[a] School of Mechanical and Aerospace Engineering, Nanyang Technological University, Nanyang Ave 50, Singapore, 639798.
[b] School of Chemical & Biomedical Engineering, Nanyang Technological University, Nanyang Ave 70, Singapore, 637457.
*Address correspondence to: lxzheng@ntu.edu.sg

ABSTRACT

Carbon nanotube (*CNT*) fibers could retain most of the intrinsic properties of individual *CNTs*, and thus have potential to enable advanced macro-scale applications, but further improvement on fiber's properties is limited by the less understanding on their failure mechanism. In this work, the strain-rate dependences of *CNT* fibers' mechanical behaviors were studied in a wide range of the tensile-strain rates. The strain-rate dependences of fibers' mechanical properties are significantly different at high strain rates and low strain rates, suggesting different failure mechanisms. It is found that tube slippage happens at low strain rates, and "cascade-like" breaking due to *CNT*'s mis-alignment dominates at high strain rates. The maximum strength of *CNT* fibers appears at high strain rates, and is mainly limited by *CNT* alignment. According to these mechanisms, improvement strategies have been discussed for obtaining reliable and high-performance *CNT* fibers.

Key words: *CNT* fiber, failure mechanism, sliding, alignment, *CNT* array, strain rate

1 INTRODUCTION

Carbon nanotube (*CNT*) fiber is a micro-scale *CNT* assembly that could retain individual *CNTs*' excellences at a larger and more practical scale level,[1,2,3,4,5] and has demonstrated potentials on enabling a wide range of advanced applications.[6] It could be fabricated by several spinning techniques, such as spinning from vertically-aligned arrays,[3, 7] cotton-like CNTs, [8] gas-phase *CNT* products of chemical vapor deposition (*CVD*),[5, 9] and solution-based *CNT* mixtures.[1,2] The fiber's properties could also be improved by post-treatments including twisting, [10] densification, [11] and cross-linking. [12] Tremendous progress has been made, but the mechanical properties of the best *CNT* fibers are still far below the theoretical values or experimental results of individual *CNTs* and small CNT bundles.[13,14] The fiber properties are found strongly dependent on the fabrication process and the starting material, with large variations in tensile strength, strain, modulus, and even mass density. Even for the same starting material, the breaking mode could be brittle breaking or ductile sliding depending on the process details.[10, 15] Therefore, studying the failure mechanism to find out key factors that limit the properties of current *CNT* fibers is becoming a critical step towards the reliable & high-performance *CNT* fibers for practical applications.

In this work, *CNT* fibers' mechanical behaviors were studied in a wide range of strain rates. The failure mechanism was discussed from the strain-rate dependences. Two different failure mechanisms were proposed to explain these observations.

2 EXPERIMENTAL

Vertically-aligned *CNT* arrays were synthesized by chemical vapor deposition (*CVD*) using argon as the carrier gas and pure ethylene as the carbon source. The *Fe* film supported by Al_2O_3 buffer layer was used as catalyst. Both catalyst annealing and *CNT* growth were performed at 750°*C* in a single-zone atmospheric pressure quartz tube furnace. *CNT* fibers were spun from the as-grown *CNT* arrays by introducing twisting with a micro-spindle mounted on a motor. Continuous *CNT* ribbons were firstly pulled out from a *CNT* array, and then passed through ethanol solution. By introducing pulling, twisting, and densification at the same time, wide ribbons were narrowed down and then packed into dense *CNT* fibers.

Scanning electron microscopy (*SEM*) was used to characterize the fractural surface of CNT fibers. The transmission electron microscopy (*TEM*) was used to characterize the morphology and microstructure of individual *CNTs*. And polarized Raman was used to measure the *CNT*'s alignment. Detail structure of individual *CNTs* was studied by transmission electron microscopy (*TEM*). These *CNTs* are multi-walled and have an average diameter of around 6~8 *nm*.

The mechanical properties of the fibers were measured on a precisely micro-loading device. The dynamic tensile testing was performed by displacement-control mode with a speed of 1×10^{-4} *mm/sec*, 1×10^{-3} *mm /sec*, 1×10^{-2} *mm /sec*, 1×10^{-1} *mm /sec*, and 1 *mm/sec*, respectively. The sample size of *CNT* fiber for all the testing is about 1.5 *cm* long with a gauge length of 5 *mm*.

3 RESULTS AND DISSCUSSION

Figure 1 shows the stress-strain curves of CNT fibers under different strain rates. All the curves include three stages: a typical linear stage at the beginning, a non-linear stage with a lower slope in the middle, and a final failure stage. A higher strain rate results in a large strength and a small fracture strain, while a lower strain rate produces a much larger fracture strain but a lower strength. For the final failure stage, it always shows brittle break at high strain rates, but both brittle break and ductile failure have been observed at low strain rates.

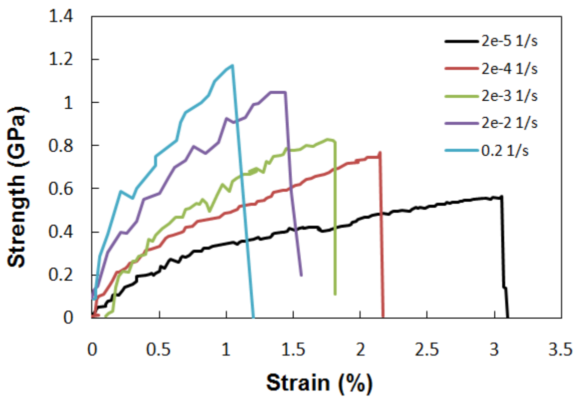

Figure 1. The tensile stress-strain curves of *CNT* fibers under different strain rates.

Figure 2 shows the strain-rate dependence of fiber strength. As the increase of strain rate, the tensile strength increase significantly, indicating a strain-rate strengthening effect. Within the used range of the strain rates, the strength can increase from 0.5 *GPa* to 1.2 *GPa*. It is also found that the strength changes significantly at low strain rate, but relatively saturates at high strain rate. If we plot the strain rate in logarithmic scale, as shown in the insets of Figure 2, it follows a power law of the strain rate.

The fiber fractures were also studied by *SEM*. We found that fibers show a sharp break at high strain rates and a gradual attenuation & pull-out break at low strain rates. The pull-out length increases with the decrease of the strain rate. Study of cyclically loading/unloading on *CNT* fibers under low strain rates is also carried out. Permanent strains (un-recoverable) were observed after several loading cycles and it further increased with increasing the peak stress and the loading cycle.

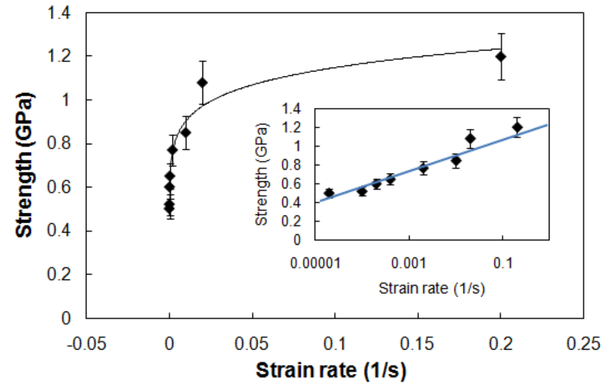

Figure 2. The dependences of strength of the *CNT* fibers on the strain rate.

These results suggest that the governing factor at low strain rates is different from that at high strain rates. A sliding-to-break mechanism happens at low strain-rate regime, while a sharp breaking is likely happened at high strain rates. At low strain rates, individual *CNTs* or small *CNT* bundles have enough time to relax through tube sliding to redistribute the strain before they break, giving a much larger breaking strain and a pull-out fracture. At the same time of sliding, interconnections between *CNTs* could be partially destroyed to realize *CNT*'s rearrangement, resulting in a low tensile strength. As the increase of strain rate, tube relaxation through sliding is becoming a slow process compared with the applied loading. The strain re-distribution becomes more and more difficult, and eventually the local strain breaks some *CNTs* and then the whole *CNT* fiber. Accordingly, a relatively sharp breaking fracture and a high tensile strength are resulted.

We have further found that the *CNT* alignment within the fibers is critical for the fiber strength at high strain rates. Because of the wavy and entangled nature of individual *CNTs* within the fibers, individual *CNTs* cannot carry load at the same time during the tensile testing, and they have no enough time to redistribute the strain through sliding at high strain rates. Therefore, some relatively straight *CNTs* will break first before those wavy *CNTs* can take the load, resulting in a "cascade-like" breaking mode (*CNTs* break one after another).

4 CONCLUSION

In conclusion, the strain-rate dependences of *CNT* fibers' mechanical behaviors were studied in a wide range of tensile-strain rates and the failure mechanisms were discussed accordingly. *CNT* fibers show a strain-rate strengthening effect. The mechanical responses of *CNT* fibers to the strain rate are different at high strain rates from low strain rates. At low strain rates, *CNT* fibers can redistribute the strain through *CNT* sliding, and sliding partially destroys the *CNT* interconnections and gives a low tensile strength; at high strain rates, tube relaxation through sliding is becoming difficult, and the fibers show a relatively sharp breaking fracture. The failure mechanism at high strain rates can be described as a "cascade-like" breaking: individual *CNTs* break serially one after another because they cannot take the load at the same time due to the imperfection in alignment. In practical, the sliding mechanism will degrade the long-term reliability of the *CNT* fibers, while the "cascade-like" breaking mechanism will limit the short-term performance (strength & modulus) of the fibers. Future improvement must deal with both tube sliding and tube alignment at the same time to obtain reliable and high-performance *CNT* fibers for practical applications.

References

1. Vigolo, B.; Penicaud, A.; Coulon, C.; Sauder, C.; Pailler, R.; Journet, C.; Bernier, P.; Poulin, P. Macroscopic Fibers and Ribbons of Oriented Carbon Nanotubes. *Science* **2000**, *290*, 1331-1334.
2. Ericson, L. M.; Fan, H.; Peng, H. Q.; Davis, V. A.; Zhou, W.; Sulpizio, J.; Wang, Y. H.; Booker, R.; Vavro, J.; Guthy, C. *et al.* Macroscopic, Neat, Single-Walled Carbon Nanotube Fibers. *Science* **2004**, *305*, 1447-1450.
3. Zhang, M.; Atkinson, K. R; and Baughman, R. H. Multifunctional Carbon Nanotube Yarns by Downsizing An Ancient Technology. *Science*, **2004**, *306*, 1358-1361.
4. Zhang, X. F.; Li, Q. W.; Holesinger, T. G.; Arendt, P. N.; Huang, J. Y.; Kirven, P. D.; Clapp, T. G.; DePaula, R. F.; Liao, X. Z.; Zhao, Y. H.; Zheng, L. X.; Peterson, D. E. and Zhu, Y. T. Ultrastrong, Stiff, and Lightweight Carbon-Nanotube Fibers. *Adv. Mater.***2007**, *19*, 4198-4201.
5. Koziol, K.; Vilatela, J.; Moisala, A.; Motta, M.; Cunniff, P.; Sennett, M.; Windle, A. High-Performance Carbon Nanotube Fiber. *Science* **2007**, *318*, 1892-1895.
6. Dalton, A. B.; Collins, S.; Munoz, E.; Razal, J. M.; Ebron, V. H.; Ferraris, J. P.; Coleman, J. N.; Kim, B. G.; Baughman, R. H. Super-Tough Carbon-Nanotube Fibres - These Extraordinary Composite Fibres Can Be Woven into Electronic Textiles. *Nature* **2003**, *423*, 703-703.
7. Li, Q. W.; Zhang, X. F.; DePaula, R. F.; Zheng, L. X.; Zhao, Y. H.; Stan, L.; Arendt, P. N.; Peterson, D. E. and Zhu, Y. T. Sustained Fast Growth of Long Carbon Nanotube Arrays for Fiber Spinning. *Adv. Mater.* **2006**, *18*, 3160-3163.
8. Zheng, L. X.; Zhang, X. F.; Li, Q. W.; Chikkannanavar, S. B.; Li, Y.; Zhao, Y. H.; Liao, X. Z.; Jia, Q. X.; Doorn, S. K.; Peterson, D. E.; Zhu, Y. T. Carbon-Nanotube Cotton for Large-Scale Fibers. *Adv. Mater.***2007**, *19*, 2567-2570.
9. Li, Y. L.; Kinloch, I. A. and Windle, A. H. Direct Spinning of Carbon Nanotube Fibers from Chemical Vapor Deposition Synthesis. *Science*, **2004**, *304*, 276-278.
10. Zhang, X. F.; Li, Q. W.; Tu, Y.; Li, Y.; Coulter, Y.; Zheng, L. X.; Zhao, Y. H.; Jia, Q. X.; Peterson, D. E. and Zhu, Y. T. Strong Carbon Nanotube Fiber Spun from Long CNT Array. *Small* **2007**, *3*, 244-248.
11. Zhang, X. B.; Jiang, K. L.; Feng, C.; Liu, P.; Zhang, L.; Kong, J.; Zhang, T. H.; Li, Q. Q.; Fan, S. S. Spinning and Processing Continuous Yarns from 4-Inch Wafer Scale Super-Aligned Carbon Nanotube Arrays. *Adv. Mater.* **2006**, *18*, 1505-1510.
12. Ma, W. J.; Liu, L. Q.; Zhang, Z.; Yang, R.; Liu, G.; Zhang, T. H.; An, X. F.; Yi, X. S.; Ren, Y.; Niu, Z. Q.; Li, J. Z.; Dong, H. B.; Zhou, W. Y.; Ajayan, P. M.; Xie, S. S. High-Strength Composite Fibers: Realizing True Potential of Carbon Nanotubes in Polymer Matrix Through Continuous Reticulate Architecture and Molecular Level Couplings. *Nano Lett.* **2009**, *9*, 2855-2861.
13. 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. *Mater. Sci. and Eng. A.* **2002**, *334*, 173-178.
14. Yu, M. F.; Lourie, O.; Dyer, M. J.; Moloni, K.; Kelly, T. F. and Rouff, R. S. Strength and Breaking Mechanism of Multiwalled Carbon Nanotubes under Tensile Load. *Science* **2000**, *287*, 637-640.
15. Zheng, L. X.; Sun, G. Z.; Zhan, Z. Y. Tuning Array Morphology for High-Strength Nanotube Fibers. *Small* **2010**, *6*, 132-137.