Failure Mechanism and Property Improvement of Carbon-Nanotube Fibers

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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, and has demonstrated potentials on enabling a wide range of advanced applications. It could be fabricated by several spinning techniques, such as spinning from vertically-aligned arrays, cotton-like CNTs, gas-phase CNT products of chemical vapor deposition (CVD), and solution-based CNT mixtures. The fiber’s properties could also be improved by post-treatments including twisting, densification, and cross-linking. 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. 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. 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 Al2O3 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 $1 \times 10^{-4}$ mm/sec, $1 \times 10^{-3}$ mm/sec, $1 \times 10^{-2}$ mm/sec, $1 \times 10^{-1}$ 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 DISCUSSION

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.](image)

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.](image)

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