# Structure and Process Dependent Properties of Solid-State Spun Carbon Nanotube Yarns

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## Introduction

We have previously reported downsizing ancient twist-based spinning technology for making continuous, densified nanotube yarns from multi-walled carbon nanotube (MWNT) forests [1]. Such nanotube yarns provide unique properties and property combinations.

Despite this important progress, the relationship between nanotube yarn properties and component carbon nanotube properties is not fully understood and processing alternatives to twist-based spinning require further exploration. The goal of this study is to obtain fundamental understanding of the origin of differences in the properties of individual nanotubes and solid-state spun nanotube yarns and to use this understanding to improve yarn properties. To achieve this ultimate goal, we have related single nanotube properties to that of nanotube yarn, investigated the effects of nanotube length and yarn processing variables on targeted properties, and investigated the properties of carbon nanotube/polymer composites.

## Experimental

Three densification methods were used for obtaining high performance MWNT yarns by forest spinning: twist, false twist, and liquid densification, as well as combinations thereof. Twist-spun yarns were produced by simultaneously applied draw and twist to ribbons drawn directly from forests of vertically oriented MWNTs [1]. The yarn diameter is controlled by the width of the ribbon from which it is spun, and measured using scanning electron microscopy (SEM). Another factor affecting yarn diameter is the areal density of the MWNT ribbon. The helix angle of the twist-spun yarn is directly related to the angle of the spinning wedge, which is controlled by the ratio of twist rate and drawing speed.

False twist is basically twisting in one direction followed by inserting approximately equal twist in the opposite direction, so that the net twist is essentially zero. As a result, nanotubes in false-twisted yarns are aligned in the yarn tensile axis direction. Liquid densification of as-drawn yarns involves imbibing a liquid and subsequent liquid evaporation, which causes the MWNT aerogel to collapse.

## Results and Discussion

Yarn strength and modulus depends upon the degree of stress transfer between nanotube bundles in a yarn, between nanotubes inside a bundle, and between walls of a nanotube. We here investigate these dependencies for forest drawn MWNT yarns that comprise ~12 nm diameter MWNTs containing ~9 walls, which are highly bundled. The average bundle contains roughly 25 MWNTs and there is wide dispersity in the degree of bundling (from one to ~60 nanotubes in a bundle) [2].

Increasing MWNT length increases the number of times a nanotube bundle can wrap around the yarn circumference and migrate between yarn surface and yarn interior, which increases stress transfer between a nanotube in a bundle and other nanotubes in the yarn, thereby increasing yarn strength. The data in Fig.1 shows measured yarn strength as a function of yarns having about the same helix angle (17° to 21°) and yarn diameter ( 5 µm to 7 µm).

We next investigated the effects of yarn diameter and helix angle on the mechanical strength of the mechanical strength of twist spun MWNT yarns. Theory predicts that the ratio of yarn tensile strength ($\sigma_y$) to the tensile strength of the component bundles ($\sigma_f$) is approximately

$$\sigma_y/\sigma_f \approx \cos^2 \alpha \, (1\text{-}k \,\mathrm{cosec}\, \alpha), \qquad (1)$$

where $k = (dQ/\mu)^{1/2}/3L$, α is the helix angle that the component fibers make with the yarn axis, *d* is the diameter of these fibers, µ is the friction coefficient between fibers, *L* is the fiber length, and *Q* (the fiber migration length) is the distance along the yarn over which a fiber shifts from the yarn surface to the deep interior and back again [3].

According to the above equation, decreasing yarn diameter should increase yarn strength. To investigate this effect, we kept yarn helix angle constant for yarn spun from a 350 µm high forest. Our results show that yarn strength substantially increases with decreasing yarn diameter, and that the slope of this approximately linear dependence is largest for yarns having the smaller helix angle.

Fig.2 shows measurement results for the dependence of yarn strength on the helix angle α obtained by twist insertion. Yarn diameter was kept relatively constant at between 18 and 20 µm. Fig.2 shows that a peak tensile strength of ~340 MPa is achievable with a helix angle of ~20° for this ~20 µm diameter yarn spun from 350 µm high forest much higher strengths result for smaller yarn diameters).

Why are these mechanical properties so much lower than those of individual small diameter SWNTs, ~37 GPa based on total nanotube cross-section for small diameter nanotubes [4,5]? The first problem is low stress transfer between outer and inner walls of individual MWNTs. Results for 1.5-20 nm diameter MWNTs show stress transfer from the outer wall to one adjacent inner wall when MWNT length is one centimeter [6]. Since our presently investigated MWNTs (<550 µm long) are much shorter than a centimeter, these results suggest that only the outer wall of our MWNTs are effective in supporting load. Since this outer nanotube wall is on average only about 14.4% of the total weight of the entire MWNT, lack of effective load transfer from the outer wall to even the first inner wall reduces MWNT specific strength by a factor of ~7. This strength penalty could be eliminated by transitioning from large diameter MWNTs to single wall nanotubes or ultra-long few-walled nanotubes.

Lack of effective stress transfer between outer and inner nanotubes in a bundle is another problem when the lengths of individual nanotubes are not sufficiently long, and this issue becomes especially important when bundle size is large, as it is for the present yarns. Consequently, decreasing nanotube bundle size is again noted as another means for increasing strength.

The major increase in strength in going from a highly oriented, forest-drawn nanotube aerogel to a yarn is a result of the ~500 fold increase in density produced by twist. In fact, the specific strength of a carbon nanotube aerogel sheets is ~130 MPa $cm^3$/g, and increases to ~460 MPa $cm^3$/g upon sheet densification. This latter specific strength is only about a factor of two lower than that of the maximum specific yarn strength reported here (1000 MPa $cm^3$/g). Moreover, large permanent twist has the disadvantage, shown in Eqn. 1 and the data of Fig. 2, of decreasing mechanical strength.

Consequently, we inquired a number of years ago in patent-related research [7] whether or not densification produced by surface tension effects or false twist can be used to increase yarn strength. This could be the case if the $k = (dQ/\mu)^{1/2}/3L$ in Eqn. 1 was very small and nanofiber length $L$ is long. The data of Fig. 2 shows that little twist is needed to maximize strength. Furthermore, the substantial strength obtained for zero helix angle (where the yarn was densified using liquid-based densification) supports the idea that inter-bundle stress transfer can be relatively high even when twist is not inserted.

Another approach for densifying nanotube yarn is to use false twist, which is much more economical to insert than true twist. Compared with the highly-oriented aerogel, which has tensile strength of ~0.2 MPa, the false-twisted yarn has a dramatically increased density and tensile strength (~113 MPa).

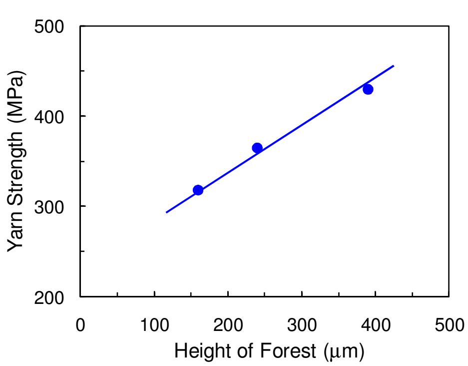


**Fig.1** Dependence of the strength of a twist-spun MWNT yarn on the height of the MWNT forests.

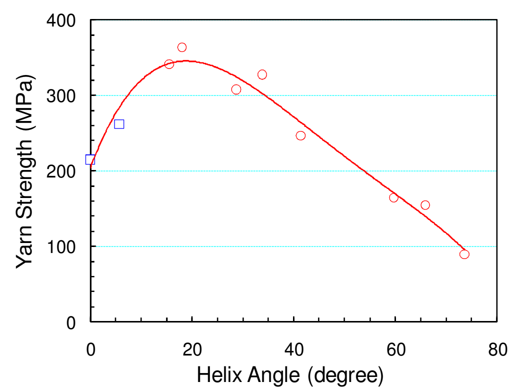


**Fig. 2** Dependence of yarn tensile strength on yarn helix angle for forest spun MWNT yarn. Yarns having very low twist (squares) were liquid densified before twist insertion, and the remaining yarns (circles) were twist spun without any prior treatment. The yarn diameter was kept constant at ~20 µm.

**Conclusions**

In this study, we investigated the effects of processing conditions and nanotube length on the properties of solid-sate spun carbon nanotube yarns. The data and analysis indicate that stress transfer between outer and inner walls of individual MWNTs, stress transfer between outer and inner nanotubes in a bundle, and stress transfer between nanotube bundles are the limiting factors for achieving higher strengths for MWNT yarns. Utilizing the understanding, we have improved the engineering mechanical strengths to 800 MPa (1 GPa $cm^3$/g for specific yarn strength) for our solid-state spun MWNT yarns. Our experimental results provide a clear path for improving mechanical strength of nanotube yarns, which involves transitioning from large diameter MWNTs to single wall nanotubes or ultra-long few wall nanotubes that are unbundled or in small bundles.

**References**

[1] Zhang M, Atkinson K R and Baughman R H, 2004 *Science* **306** 1358
[2] Zhang M, Fang S, Zakhidov A A, Lee S B, Aliev A E, Williams C D, Atkinson K R and Baughman R H, 2005 *Science* **309** 1215
[3] Hearle J W S, Grosberg P, Backer S, *Structural Mechanics of Fibers, Yarns, and Fabrics*, vol. 1 (Wiley, New York, 1969)
[4] Yu M-F, Files B S, Arepalli S, Ruoff R S, 2000 *Phys. Rev. Lett.* **84** 5552
[5] Walters D A *et al.*, 1999 *Appl. Phys. Lett.* **74** 3803
[6] Hong *et al.*, 2005 *Proc. Natl. Acad. Sci. USA* **102** 14155
[7] "Fabrication and Application of Nanofiber Ribbons and Sheets and Twisted and Non-Twisted Nanofiber Yarns", M. Zhang, S. Fang, R. H. Baughman, A. A. Zakhidov, K. R. Atkinson, A. E. Aliev, S. Li, C. Williams, Filed PCT Int. Application (2007), 425 pp, CODEN:PIXXD2 WO 2007015710 A2 20070208.