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# Mechanical and electrical property improvement in CNT/Nylon composites through drawing and stretching

Xin Wang [a], Philip D. Bradford [a], Wei Liu [a], Haibo Zhao [a], Yoku Inoue [b], Jon-Paul Maria [a], Qingwen Li [c], Fuh-Gwo Yuan [a], Yuntian Zhu [a,*]

[a] North Carolina State University, 911 Partners Way, Raleigh, NC 27695, USA
[b] Shizuoka University, Johoku, Hamamatsu 432-8561, Japan
[c] Suzhou Institute of Nano-Tech and Nano-Bionics, Suzhou 215123, China

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ABSTRACT

The excellent mechanical properties of carbon nanotubes (CNTs) make them the ideal reinforcements for high performance composites. The misalignment and waviness of CNTs within composites are two major issues that limit the reinforcing efficiency. We report an effective method to increase the strength and stiffness of high volume fraction, aligned CNT composites by reducing CNT waviness using a drawing and stretching approach. Stretching the composites after fabrication improved the ultimate strength by 50%, 150%, and 190% corresponding to stretch ratios of 2%, 4% and 7%, respectively. Improvement of the electrical conductivities exhibited a similar trend. These results demonstrate the importance of straightening and aligning CNTs in improving the composite strength and electrical conductivity.



## 1. Introduction

Carbon nanotubes (CNTs) have highly desirable mechanical, thermal and electrical properties. They are promising candidates as reinforcement for the next generation of high performance composites. Significant effort has been focused on developing CNT composites over the last two decades. Methods for fabricating CNT composites include: dispersing short CNTs in polymer matrix [1–3], infiltrating CNT buckypaper with polymer solutions [4,5], and reinforcing with CNT fiber assemblies [6–8].

Studies of CNT composites [9–11] so far have largely focused on improving the nanotube dispersion quality and the interface with the matrix. To achieve good quality CNT/polymer dispersion, short CNTs in low volume fractions are typically utilized. Although short CNT composites have some advantages in certain low volume fraction applications, such as thermally and electrically conducting materials, their mechanical properties fall far short of traditional high performance structural composites. It results largely from the short CNT length (usually <10 μm), which cannot efficiently transfer a mechanical load across the weakly bonded interface. Chemical modification may improve interfacial shear strength, at the expense of introducing defects in the CNT structures and thus degrading the properties [12]. Achieving high volume fractions of dispersed CNTs in polymer is difficult because the resulting high viscosity complicates further processing.

Another approach is to infiltrate CNT films (also known as buckypapers) with thermoplastic polymers or epoxy resin [4,13]. The CNTs in the buckypaper sheets have no preferential orientation and each nanotube is curved and wavy. CNT fibers (yarns) can also be used to fabricate composites. They include plied or braided CNT fiber assemblies [6,7] and long spun fibers infiltrated by polymer [8]. The most significant component in these composites is the CNT fiber. Techniques for making CNT fibers are classified into "liquid" methods [14], where CNTs are dispersed into a liquid and solution-spun into fibers, and "solid" methods [15,16], where CNTs are directly spun into ropes or yarns. The last 10 years have seen rapid progress in the "solid" fiber spinning approach [17–24]. While the mechanical properties of these fibers are promising, they both have limitations. The "liquid" method requires short CNTs for solution spinning, which limits the mechanical properties, while the "solid" method involves fiber twisting, which is a slow and expensive process. Scaling-up of these technologies presents a major obstacle for engineering applications.

In a recent work by Cheng et al. [25], a high volume fraction of highly aligned CNTs was homogeneously dispersed in an epoxy matrix. The CNT/epoxy composites were produced by drawing and stacking CNT sheets from aligned CNT arrays, and then infiltrating the stacked CNT sheets with epoxy. This method alleviates

* Corresponding author. Address: Room 240, 1001 Capability Dr. Raleigh, NC 27606, USA. Tel.: +1 919 513 0559; fax: +1 919 515 3419.
*E-mail address:* ytzhu@ncsu.edu (Y. Zhu).

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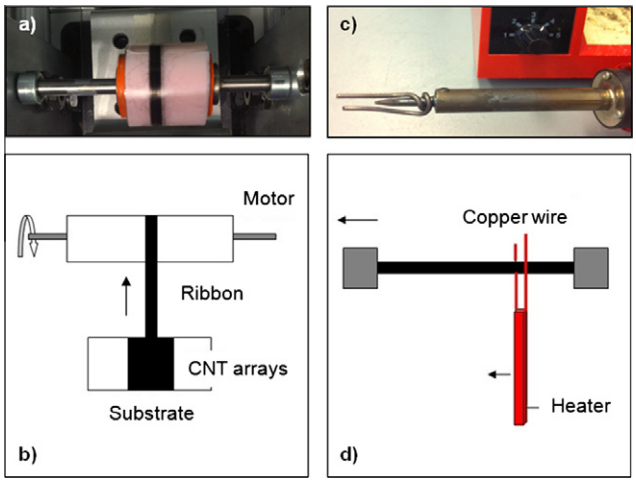


**Fig. 1.** (a) Rotary winding device. (b) A schematic of the drawing and winding process. The nylon solution was added on the as-wound ribbons using a dropper. (c) A piece of copper wire attached to a heating device provided local heating of the CNT composite. (d) A schematic of the local heating and stretching process.

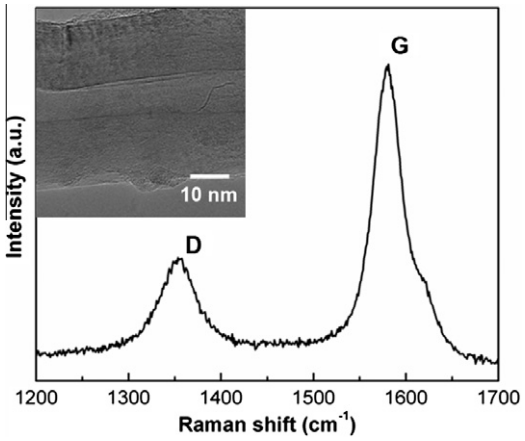


**Fig. 2.** Raman spectrum of the CNTs prepared by one-step CVD method [26] and used to make CNT composite in this study. The inset is a TEM image of a thick-walled CNT that was used in this study.

many limitations of other CNT processing methods. However, wavy nanotubes are still present, which reduces the mechanical properties of the composites.

Here we report a strategy, mechanical stretching of aligned CNT composites, to address the issue of CNT waviness. This approach involves drawing and winding thin CNT ribbons from free-standing CNT arrays, infusing a nylon 6,6 solution between layers of the CNT ribbon without disturbing the pre-existing alignment and stretching the composite while locally heating it to reduce the CNT waviness. The mechanical and electrical property results of this work identify a new mechanism of maximizing mechanical properties of CNT composites.

## 2. Experimental

### 2.1. Rotational winding CNT ribbons into composites

Vertically aligned CNT arrays with a height of ~700 μm were synthesized on a quartz substrate with iron chloride ($FeCl_2$) powder using a thermal chemical vapor deposition (CVD) method described in literature [26]. The CNTs were drawn from the arrays onto a rotating cylindrical polytetrafluoroethylene (PTFE) spool (as depicted in Fig. 1a and b). Continuous CNT tows were placed on the rotating spool while tension was applied in order to well pre-align the ribbons. Meanwhile, nylon 6,6 (1.14 g/cm$^3$ at 25 °C, molecular weight = 262.35, Sigma Alderich) solution (1 wt.% in phenol) was infused between the layers of the as-wound CNT ribbons using a dropper. After approximately one hundred winding revolutions at a speed of 1.1 m/min, unidirectional CNT/nylon 6,6 composites (10 cm long, 0.5 cm wide and 20 μm thick) were produced.

### 2.2. Locally heating and stretching the CNT composites

The as-wound CNT/nylon 6,6 composite was removed from the PTFE spool. Precise stretching was performed on a tensile testing machine (Shimazu EZ-S). The composite was locally heated by a fabricated heating element with dual prongs. The temperature between the two extended wire ends (see Fig. 1c and d) reached approximately 160 °C, which was measured by a thermocouple. The heating element moved along the composite at a speed of 3 mm/s so that the composite was heated and stretched uniformly along the length direction at a speed of 0.1 mm/min. The low applied load and the moving local heating source ensured that the whole composite was uniformly stretched without premature failure. The stretched CNT composites were hot pressed in a vacuum oven at 160 °C for 1 h.

### 2.3. Materials characterization and testing

Tensile test specimens were cut from the CNT/nylon 6,6 composite films into strips with dimensions of 10 mm long and 0.3 mm wide. CNT alignment was parallel to the longitudinal direction of the tensile loading. Edge defects were minimized by cutting the sample with a sharp razor and then hot-pressing it at 160 °C, which allowed the polymer molecules to partially reconfigure to smooth sample edges. Sample width was measured using a calibrated scale bar in an optical microscope (30×) and the sample thickness was measured using a micrometer. The composite specimens with gauge length of 6 mm were tested at room temperature using the tensile testing machine at a crosshead speed of 0.5 mm/min. Five specimens were tested for each CNT/nylon 6,6 composite. Resistance was measured using the four-probe method. Transmission electron microscopy (TEM) analysis of the nanotubes was performed using a JEOL 2010F microscope at an acceleration voltage of 200 kV. Scanning electron microcopy (SEM) analysis of the ribbons and composite fracture surface was carried out on a JEOL 6400F microscope with an acceleration voltage of 5 kV.

**Fig. 3.** A photograph of the flexible CNT/nylon 6,6 composite film (before stretching) made by the drawing and winding method.