



## Stabilizing carbon nanotube yarns using chemical vapor infiltration



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### ABSTRACT

Carbon nanotube (CNT) yarns exhibit high strength, low density, and relatively good conductivity and piezoresistivity, which makes them an ideal candidate for many advanced applications such as reinforcements for multifunctional composites. However, CNT yarns usually lack the required property stability under load. In this paper a method for stabilizing CNT yarn using chemical vapor infiltration (CVI) to infiltrate and deposit pyrocarbon into CNT yarns is reported. The deposited pyrocarbon effectively binds neighboring CNTs to inhibit inter-nanotube sliding under load, which consequently stabilize the CNT yarns. Relaxation tests showed that compared to pristine CNT yarns, the stabilized yarns have higher electrical stability as well as load retention (~93% versus ~61%). There was also a concomitant increase in density along with improved electrical conductivity, mechanical strength and stiffness. Furthermore, under sonication the CVI treated yarns resisted disintegration, making them suitable for electrochemical applications.

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### 1. Introduction

Carbon nanotubes (CNTs) have been processed into various forms such as yarns [1], ribbons [2], and composites [3] for different potential applications. In particular, CNT yarns have been studied extensively due to their potential as a structural and multifunctional material of the future [4–10]. CNT yarns have been produced by spinning from a wet solution [2], dry-spinning directly from an array [1] or CNT aerogel [11]. The mechanical properties of CNT yarns have been extensively studied with strengths ranging between 300 MPa to 3.8 GPa [12], and stiffness ranging from 30 to 275 GPa [13]. CNT yarns have been found to have good electrical conductivity [14] with reported values between 150 to 8300 S/cm. [15].

Numerous applications for CNT yarns have been suggested so far, some of them being strain sensors [4], electrical conductors [5,16], structural reinforcements [17,18,10], field emitters [7] and electrochemical actuators [9]. All of these applications would require good electrical or mechanical stability. The piezoresistive properties of CNT's combined with the ability to produce yarns of dimensions in the same order of carbon fibers make CNT yarns an

attractive candidate for non-invasive *in situ* strain sensors. The relatively high electrical conductivity of yarns is also a favorable characteristic for conductive composites. Under load the nanotubes within the yarn slide past each other, which leads to permanent elongation and a high degree of stress relaxation. Consequently, the mechanical and electrical properties of the CNT yarns also alter under load, which is not acceptable for most applications. Therefore, it is important to stabilize the CNT yarns.

In this work the stability of the CNT yarn is improved which is a requirement for practical electrical and mechanical application by means of chemical vapor infiltration (CVI) of carbon. Tests to investigate the yarn stability were primarily performed. Additionally, other aspects such as growth, failure mode, mechanical and electrical properties of the CVI and pristine yarns were investigated.

### 2. Experimental

The vertically aligned MWCNT arrays were grown on a quartz substrate by the “chloride mediated chemical vapor deposition (CVD)” method [19]. Typically, a substrate that was 75 mm long and 25 mm wide was cleaned by ethanol and placed at the center of a horizontal quartz tube furnace. Acetylene was used as carbon source and FeCl<sub>2</sub> powder was used as catalyst. CNT growth was carried out at the temperature of 760 °C at 3 Torr. The as-synthesized MWCNTs had a height of 1.1 mm, an outer diameter of ~50 nm and approximately 40 walls. The array height was measured using a calibrated scale bar in an optical microscope (30×). The diameter of the MWCNTs was measured using the ImageJ

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software, based on the transmission electron microscopy (TEM) images acquired by a JEOL 2000FX TEM operated at 200 kV.

The aligned CNTs were spun into yarns using a solid state spinning process by simultaneous drawing and spinning. The CNT ribbon was maintained at 3 mm width during the spinning process. The twist angle was verified with the SEM and was maintained between 30° and 35°. A yarn diameter of about 40 μm was maintained and was measured using laser diffraction method [20]. After the spinning process the yarns were placed on a silicon substrate which was then placed into a high temperature quartz tube furnace for CVI treatment.

The entire CVI process was carried out at atmospheric pressure; argon and hydrogen were passed through the quartz tube chamber at 50 sccm and 10 sccm respectively after evacuating the tube with a low pressure pump. Once the temperature reached 750 °C, ethylene, the source gas for pyrocarbons was passed through the tube at 30 sccm. The infiltration process was carried out for time periods of 5 min, 30 min, 1 h and 2 h respectively for the CNT yarns samples. After infiltration, the furnace and the supply of ethylene were switched off and the atmosphere of argon and hydrogen was maintained until the furnace was cooled down. Finally, argon was used to purge the tube.

The yarns were removed, cut and affixed to paper tabs with 5.5 mm gage length for mechanical, electrical and electromechanical tests. A Shimadzu EZS tensile tester with a 2 N load cell was used for mechanical measurements and an Agilent 34410 A multimeter was used for standard 4-probe electrical measurements. For electromechanical measurements, copper wires were attached to the CNT yarns on the gage paper using silver epoxy and electrical measurements were made simultaneously while under tensile loading. Raman spectroscopy was carried out using Rainshaw Ramascope spectroscopy to identify the nature of microstructure. For relaxation experiments the Shimadzu EZS tensile tester was used to apply the tensile load. The machine was stopped and its relaxation was recorded manually by recording the force on the load cell at set time intervals. The electrical measurements were recorded using Agilent 34410 A. A Mettler XP2U Ultra-microbalance with a sensitivity of 0.0000001 g was used to measure the weight of the yarns and the density was measured as mentioned by Miao [15].

### 3. Results and discussions

Some of the techniques developed for the post-processing of CNT yarns to enhance their properties include liquid densifications of yarns, annealing [13] and laser sweeping [21]. Chemical Vapor Infiltration (CVI) involves the vapor phase infiltration and subsequent deposition of matrix into porous structures. The CVI technique has been extensively used in the processing of ceramic composites [22] and in production of carbon fiber-carbon composites [23]. Deposition of carbon in micro-fiber preforms generally occurs on the fiber surface. Precise conditions must be met so that the pyrolyzed carbon does not preferentially deposit on the surface, close off the fabric pores. The CVI technique has also been used to produce aligned CNT-Carbon composites from CNT arrays [24] and aligned CNT reinforced silicon carbide composites [25]. Bradford et al. [26] studied the compressive properties of CNT foams produced by CVI of CNT arrays. Carbon deposition can also be obtained by polymer pyrolysis which requires multiple polymer deposition and pyrolysis cycles. Tests conducted by Gong et al. [24] suggested that the nature of pyrocarbon deposited on CNTs by CVI from a propylene source is rough laminar and anisotropic. Rough laminar pyrocarbon among other things has a more oriented crystal structure and higher strength than glassy isotropic carbons.

Electrical and mechanical relaxation tests were performed to test the stability of the yarn over time. Ideal sensors do not have any resistance drift with time. The pristine yarn and CVI treated yarn were loaded up to 50% of their mechanical strength after which both the load retained and resistance were recorded with respect to time as shown in Fig. 1(a). After 5 h, retention in load was 93.2% for CVI yarns compared to only 60.8% for pristine yarns. Similarly, a large drop in resistance occurred for pristine yarns as shown in Fig. 1(b). This resistance drift is undesirable for applications where stable electrical conductivity is required. In contrast, the CVI yarns had a relatively stable resistance value during constant loading.

Fig. 1(c) is the plot of force versus strain which also includes unloading of the yarn (dashed lines) after relaxation shown in Fig. 1(a) and (b). This plot shows that pristine yarn exhibits a large permanent elongation of about 2.5% after unloading. This permanent elongation is due to the sliding of the nanotubes within the yarn under load, which consequently leads to relaxation in load as seen in Fig. 1(a). However it was very minimal in the CVI yarns with a permanent elongation of only .03% strain. Within the CVI yarns, the nanotubes cannot slide as freely. Mechanical properties of pristine yarn after removal of relaxation load showed higher stiffness within the regime of the relaxation load. Beyond this load for the pristine yarn the stiffness reduced. The relaxed yarn showed overall reduced strain to failure: during loading for relaxation the strain was ~3.6%, however, on tensile testing of the relaxed specimen the total strain to failure was 1.9%. The CVI yarn on loading however showed a relatively constant stiffness and strain after removal of relaxation load.

Fig. 2(a) and (b) shows the plot of force versus strain for pristine and CVI yarns respectively, cycled 10 times at ~50% of mechanical strength before loading to failure. The permanent elongation in the pristine yarn after 10 cycles (loading to 50% mechanical strength) was 2.46%, whereas for the CVI yarn under the same conditions as above the permanent deformation was only 0.17%. This lower drift in strain further supports the conclusion made in the previous sections about lower sliding of the CNTs under load and consequently better load transfer.

Additionally, CVI yarns resisted sonication in ethanol solution. The pristine CNT yarn disintegrated within 30 min while even after sonication for 3 h the CVI yarn would not segregate. While this can be observed in a CNT/Polymer composite yarn, the conductive nature of the carbon matrix makes electrochemical application possible.

To better understand this, the yarns were infiltrated for different treatment times, i.e. pristine, 5 min, 30 min, 60 min and 120 min. Surface SEM images of yarns infiltrated over different time durations are shown in Fig. 3. A linear increase in diameter was observed as growth time increases until 60 min after which the growth rate leveled.

The fracture surface was studied and the SEM images are shown below in Fig. 4. The diameter of the coated CNTs showed an increasing trend with increasing treatment times similar to those of the surface images. Even after short treatment time such as 5 min, a discernible increase in diameter was observed (Fig. 4(a) and (b)). After longer treatment times of 1 h and 2 h pyrocarbon formation developed around multiple nanotubes and finding individual nanotubes in isolation was progressively harder.

Fig. 5(a) and (b) reveals that for pristine yarns nanotube sliding largely occurred during fracture while in CVI yarns the fracture was more brittle with less sliding. The fracture surface in Fig. 4(e) and (f) revealed distinct sword and sheath formations, where the CNT was enveloped by a larger pyrocarbon matrix. The observation of the fracture surface revealed that during failure under tensile load the pyrocarbon matrix fractures, indicating relatively low strength of the pyrocarbon matrix while CNTs do not

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