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Carbon nanotube yarn strain sensors

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Abstract
Carbon nanotube (CNT) based sensors are often fabricated by dispersing CNTs into different types of polymer. In this paper, a prototype carbon nanotube (CNT) yarn strain sensor with excellent repeatability and stability for *in situ* structural health monitoring was developed. The CNT yarn was spun directly from CNT arrays, and its electrical resistance increased linearly with tensile strain, making it an ideal strain sensor. It showed consistent piezoresistive behavior under repetitive straining and unloading, and good resistance stability at temperatures ranging from 77 to 373 K. The sensors can be easily embedded into composite structures with minimal invasiveness and weight penalty. We have also demonstrated their ability to monitor crack initiation and propagation.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The excellent piezoresistive property of individual carbon nanotubes (CNT) has been demonstrated by several groups [1–5]. These studies generally involved measuring the conductivity of individual CNTs under strain using an AFM tip or a micro-electromechanical device. Although individual CNTs exhibit exciting properties for potential application as sensors, in reality, integrated CNT-based nano-sensors have not been realized due to the challenges associated with their integration into bulk structures. Assembling these nano-sensors into microscopic sensors for easy integration into bulk structures is important for practical applications. Some success has been reported on scaling up these nano-sensors by dispersing them into polymers via different approaches [6–12]. These methods have at least one feature in common: the sensor fabrication involves dispersing a small amount of CNTs into a polymer matrix to form a 3D CNT network for electron conduction. The addition of CNTs dramatically increases the conductivity by forming electric pathways in the otherwise insulating polymer [13]. As such, the composite itself can sense strain under loads by monitoring the resistance change.

Recent research in developing CNT-based strain sensors has generated some excitement, because CNTs, as compared to traditional strain sensors, offer the potential of being embedded within composite structures for *in situ* measurement. Due to their high strength, small diameter and light weight, CNT-based sensors can overcome several limitations of the existing conventional sensors, including limited monitoring locations, fixed directions and separation from the structure that is being monitored. However, several challenges still remain before CNT-based sensors are fully implemented into real structures.

Two significant issues that need to be addressed are repeatability and stability. Repeatability refers to repeatable resistance–strain behaviors under cyclic service conditions and stability refers to stable resistance. The resistance of CNT/polymer film sensors have been observed to change over time even without an applied mechanical load [8, 9], which poses a serious problem in practical applications. Resistance drifting may result from defects and breakdown of the shell structure of the CNTs [14], as well as heating from electric currents passing through the CNT sensors [8]. In addition, CNT composite strain sensors were found to exhibit resistance hysteresis in a cyclic strain loading [6, 11, 12], which indicates

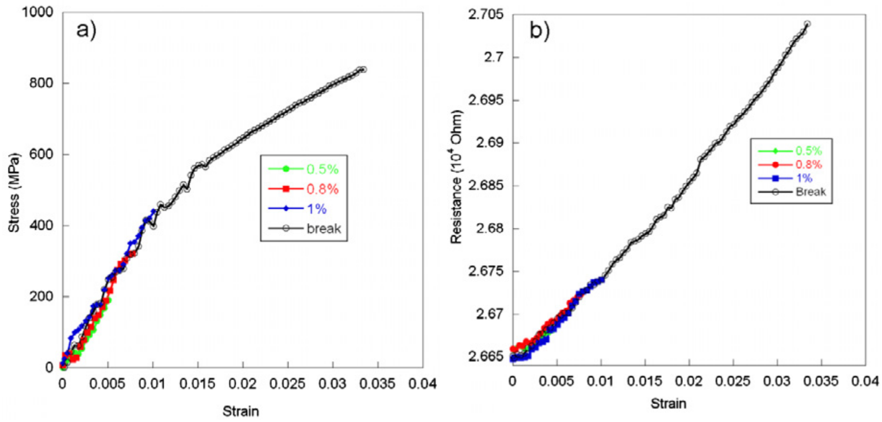

Figure 1. Repetitive testing of pure dry CNT yarns showing repeatable stress–strain and resistance–strain behaviors up to 1% strain: (a) tensile stress–strain curve, (b) *in situ* resistance measuring during the tensile stretching. Pure dry yarns underwent loading and unloading sequentially to strains of 0.5%, 0.8%, 1% and break, respectively and the resistance was measured *in situ*. After each loading, the yarns were completely unloaded before the next loading.

irreversible deterioration of the CNT/polymer interfaces. CNT buckypapers have also been used as strain gauges [14–16]. However, due to their very low strength and permanent deformation after a strain of approximately 0.04%, they are not ideal for applications that require multi-functionality or repeatability. CNT yarns have been reported as actuators and sensors when they were immersed in electrolyte and charged at high voltage [17]. However, it is not convenient to embed yarn sensors with electrolyte in composites. Here we report using pure CNT yarns directly as piezoresistive strain sensors which could be readily incorporated in composites for *in situ* health monitoring. The yarns do not require any chemical grafting or charging to work as sensors. To our knowledge, this is the first report of using the piezoresistive properties of pure CNT yarns to make strain sensors.

2. Experimental procedure

2.1. CNT yarn spinning and diameter measurement

CNT arrays were grown using a CVD method described before [18]. CNT ribbons approximately 3 mm wide were pulled out from an CNT array (grown on silicon substrates) by hand using flat tweezers and then attached on a spindle using a piece of double-sided tape. A CNT yarn was spun by a rotating spindle that was moved away from the array at the same time. The rotating speed was 7000 rpm and the yarn take-up speed was about 2 mm s^{-1}. The diameters of the as-spun yarns were 3–30 μm and were controlled by the width of ribbons initially pulled out from the array. The yarn diameters were measured using a laser diffraction method, whose accuracy was verified by diameter measurements in a SEM.

2.2. Electrode deposition for dry yarns

CNT yarns were collected on sandpapers with a rectangular slot cut out, as shown in figure 1(c). Yarns in the slot region were covered by a plastic film to protect them from deposition and the exposed parts were coated with a 5 μm thick aluminum layer using magnetron sputtering in pure Ar at a pressure of 2×10^{-3} Torr. The sputtering power was 40 W. Silver paste was used to connect two thin copper wires with yarns that were covered by the sputtered aluminum contacts. The gauge length of the yarns was 10 mm for *in situ* resistance measurement during mechanical testing.

2.3. Composite strain sensors fabrication

CNT yarns were attached on a piece of release film that is commonly used for vacuum bagging of composites. High conductive silver colloid was dropped on the ends of the yarns to form electrodes. The resin system (59% EPON™ Resin826, 21% EPIKURE™ 9551 Curing Agent, 20% Heloxy™ Modifier62 in weight per cent, purchased from Hexion) was mixed using a magnetic stirrer. Bubbles trapped in the resin were removed by degassing in a vacuum oven. Resin was cast on the yarns to form thin films and, after curing at 373 K for 3 h, an integral structure of composites with built-in yarn sensing elements was produced. The composite thin films, around 100 μm in thickness, were cut into coupons using a razor blade. Two copper wires were soldered on the silver electrodes for resistance tests.

2.4. Characterization

SEM images of the CNT yarns were taken using a JEOL 6400F at 5 kV and a working distance of 15 mm. An EZ-S tensile tester with a 2 N load cell for pure dry yarns and a 100 N load cell for composite sensors was used for mechanical testing. An Agilent 34410A digital multimeter was used to measure the resistance across the yarn sensors. The sample gauge length for electromechanical testing was 1 cm. The samples were loaded under tension and the resistance change was recorded in real time.

3. Results and discussion

Pure CNT yarn can be utilized as a superior novel piezoresistive sensor with excellent repeatability and stability

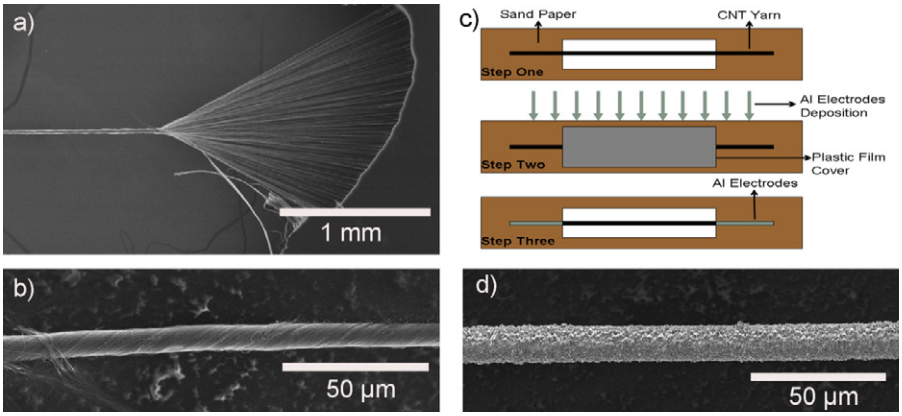

Figure 2. CNT yarn spinning and deposition of Al electrodes on CNT yarns. (a) SEM of directly spun CNT yarns from the as-grown CNT array. (b) Low magnification SEM of an as-spun yarn. (c) Schematic drawing of Al electrode deposition on dry CNT yarns using magnetron sputtering. (d) Low magnification SEM of a yarn end coated with Al.

for structural health monitoring. The electrical resistance, as a function of elastic strain, of CNT yarns was measured *in situ* during mechanical testing. Both the resistance and the stress of the yarn have a linear behavior with strains up to 1%. The resistance–strain behavior is repeatable, with no hysteresis, as shown in figure 1. The CNT yarn itself is a macroscopic CNT assembly that offers an electric pathway along its longitudinal direction, as shown in figure 2. Carbon nanotubes within a yarn have good contact with their neighbors due to the twisting process during the yarn spinning. Radial inward forces provide close contact and load transfer between CNTs during tensile loading of the yarn.

The resistance of the yarns monotonically increased with increasing strain. There are two factors that affect the resistance of a yarn during tensile strain: one is the strained individual CNTs; the other is the improved contact between CNTs and their neighbors due to the contracting radial force produced in the yarns. The latter is obviously not the reason for the resistance increase since improved contact should decrease the resistance. Due to this fact, it appeared that the resistance increase with strain was caused by the strained individual CNTs.

It has been established by several pioneering experiments [1–5] that the resistance of CNTs changes when subjected to strain. A generic equation (1) provides useful insights for understanding the resistivity of individual CNTs. Specifically, the total resistance (R_{tot}) is:

$$R_{\text{tot}} = R_s + \frac{1}{|t|^2}\frac{h}{8e^2}\left[1 + \exp\left(\frac{E_{\text{gap}}}{kT}\right)\right] \qquad (1)$$

where R_s is the contact resistance between the electrodes and the CNTs, which is negligible since the electrodes have good contact with the yarns, $|t|^2$ is the transmission probability of electrons across the band gap barrier, T is the temperature, h, k, e are constants and E_{gap} is the band energy gap. The validity of equation (1) has been verified experimentally for individual CNTs under loading [1–5]. The CNT yarn sample contains hundreds of thousands of individual CNTs. Therefore, the resistance increase shown in figure 1 is a collective behavior of all CNTs in the sample. In other words, figure 1 and equation (1) indicate that the band gap energy of most individual CNTs in the yarns increased under tensile strain, which led to a collective resistance increase across the yarn.

As discussed earlier, it appears that the improved contact between individual CNTs in the yarn with strain had only a minor impact on the yarn resistance. Unlike dispersed CNT composites where each CNT may have only a few contact points with other CNTs for electric conduction, the CNTs in the yarns are packed closely and have thousands of contact points with their neighbors along their whole length; these provide a large total contact area for electron hopping between CNTs. Therefore, the increase in contact area within a yarn under tensile loading will not provide much further improvement in electric conduction because the contact area is already large.

The excellent repeatability of resistance–strain behavior under cyclic loading (see figure 1) was also related to the large contact area between the CNTs. The close contact with large contact area along the whole CNT length, the large van der Waals force between CNTs and the radial inward force produced during loading provide good structural stability for the yarns during the loading and unloading in the elastic region, which gives the yarns excellent resistance–strain repeatability.

The sensitivity of the strain gauge is termed as the gauge factor (GF), and is described by equation (2):

$$\text{GF} = \frac{\Delta R/R}{\Delta L/L} = \frac{\Delta R/R}{\varepsilon}. \qquad (2)$$

The gauge factor of pure yarns was around 0.5. Single nanotubes have a gauge factor of hundreds depending on the structure of the nanotube [2]. Why was the gauge factor of yarns made of individual nanotubes much lower than single nanotubes? Yarns are made of billions of short individual CNTs with lengths of around several hundred micrometers. The contact resistances between nanotubes are much larger than the resistance of the nanotubes themselves. A detailed discussion is given in the following paragraphs. The total resistance across a yarn is described by equation (3).

$$R = R_1 + R_2. \qquad (3)$$

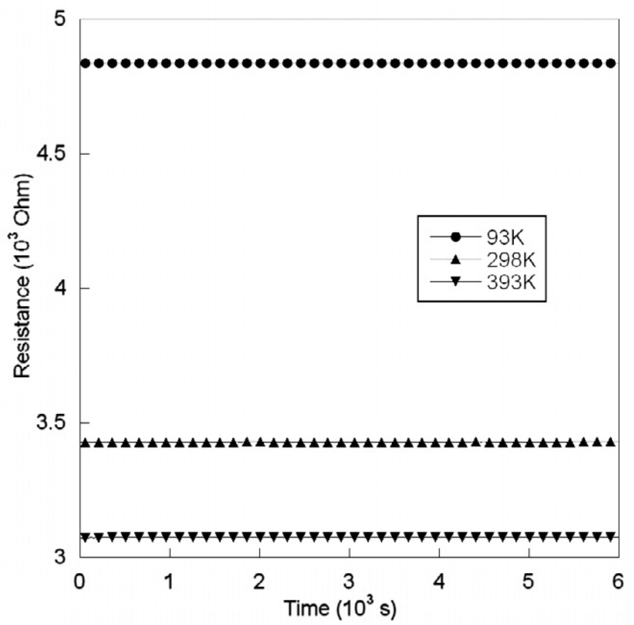

Figure 3. Stability testing of yarn sensors under zero-load conditions showing that the resistances were very stable at three different working temperatures: immersed in liquid nitrogen, at room temperature and annealed at 393 K in an oven. The measurement was made in a continuous mode.

The total resistance consists of two parts, R_1 and R_2. R_1 is the actual total electron conducting resistance along the length of each nanotube. R_2 is the total resistance of electron hopping from nanotube to nanotube. This is a result of the finite length of CNTs within the CNT yarns. Usually, the conductivity of the CNT assembly is two orders of magnitude smaller than individual CNTs [19, 20]. With the above discussion, we are ready to further assess the nature of the sensitivity of CNT yarns.

In the studied yarns, the resistance change is from R_1. As discussed previously, no improvement of electric conduction was observed during the loading since CNTs in the yarn already have a large contact area. During loading, R_1 changes, while R_2 remains constant. From equation (4), a combination of equations (2) and (3), it is clear that the yarns will have a smaller gauge factor than that of the single CNTs since R_2 accounts for the majority of the resistance measured in yarns.

$$\mathrm{GF} = \frac{\Delta R/R}{\Delta L/L} = \frac{\frac{\Delta R_1+R_2}{R_1+R_2}}{\varepsilon}. \tag{4}$$

The resistance of the yarn sensors showed good stability during 100 min of measurements at −196, 25 and 110 °C, as shown in figure 3. Samples were immersed in liquid nitrogen, kept in the oven and held at room temperature respectively for continuous real-time resistance testing under zero-load conditions. The observed stability holds the promise for the sensors to function over a large range of temperatures.

The good stability of yarns sensors was a result of the ultralow heat producing power, relatively large surface area for heat dissipation, and steady contact and large contact area between CNTs in the yarn. In the present experiments, the test current was 100 μA for the 10 kΩ range. As a result, the power of heat producing of the yarn resistor was around 10^{-5} W. Thermal stability of CNT yarns heated by electric current was shown in a recent paper and no temperature increase was detected in the CNT yarn when a current of 30 mA was used [21]. The stable resistance shown by CNT yarns over a wide range of temperatures will be critical to the real application as strain sensors. As shown in equation (1), the resistance of CNT-based sensors can change exponentially with the temperature. An unstable resistance under static testing was reported in a CNT/polymer strain sensor fabricated using the dispersion method; the resistance was found to decay exponentially during testing [8]. The yarns not only have a stable temperature when a testing voltage is applied, but also have a stable electric current conducting path. The large contact area between CNTs prevents charge-induced contact deterioration. Sensors fabricated by dispersing CNTs in a polymer have few contact points and the large current concentration and subsequent localized heating may lead to damage. In contrast, CNTs in the yarn have large contact areas, leading to less localized heating and thus better long term resistance stability.

To demonstrate the concept of integral composite sensors, CNT yarns were embedded into epoxy resin. The electric conduction mechanism in yarn composites was different from traditional CNT composites fabricated by dispersing CNTs into polymers. Traditional CNT composite strain sensors require the addition of a certain amount of CNTs to reach the electrical percolation threshold. Electrons conduct through the 3D CNT networks formed through the whole composites. In contrast, in yarn composite sensors, the electric current only passes through the CNT yarns and the surrounding matrix remains electrically insulating. This is analogous to inserting an electric wire in a composite that has a diameter of one tenth of a human hair. Carbon nanotube yarns can be seamlessly used in composite structures since they are minimally invasive to the composite structure and have negligible added weight because of their low density [22].

As shown in figure 4(a), the resistance change was linear with strain as the composite sample was loaded in the longitudinal direction, while very little resistance change was observed when loaded in the transverse direction. The applied load was transferred to the CNT yarn, which changed the conductivity of the yarn. The overall increase in resistance under transverse loading of the yarn was attributed to the off axis CNT twist angle in the yarns. The twist in the yarns ensured that the individual CNTs were subjected to some tensile strain even in the transverse loading case.

The longitudinal GF of the strain sensor was about 0.38 and remained constant over the whole strain range. The transverse GF ranged from 0.02 to 0.04. Compared to the longitudinal resistance change, the transverse resistance change could be neglected. The composite sensor has a unidirectional sensing property in the yarn alignment direction. This observation could help engineers to not only detect the load that the structure is undergoing, but also determine the direction of the external force applied by utilizing multiple CNT yarn sensors oriented in different directions.

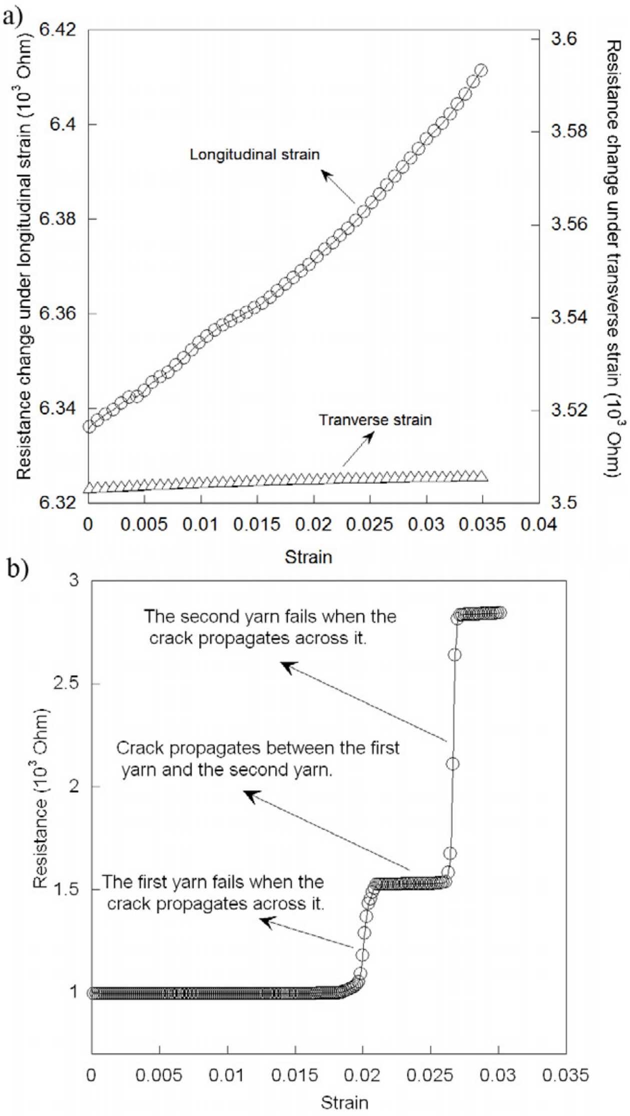

Figure 4. *In situ* monitoring of strain and crack propagation in a composite structure. (a) Linear increase of resistance when the composite structure was under longitudinal tension, and non-linear increase under transverse tension; (b) crack propagation was easily monitored by building multiple CNT yarns in the composite structure.

The initiation of micro-cracks and the crack propagation in the composites were detected by aligning multiple yarns in the composites. As shown in figure 4(b), an initial sharp crack was deliberately cut at the edge of the composite sample. The crack propagated across the sample under loading. Tremendous resistance changes were observed when the crack approached the yarn sensing elements. As the crack continued propagating, yarns were broken sequentially. The breakage of the yarns caused a sharp increase in the total resistance. The results provided here hold promise for the application of detecting cracks in traditional composite structures using embedded CNT yarn sensors. The early detection of small internal cracks could allow for early maintenance to prevent potential catastrophic failure.

4. Conclusion

In conclusion, it has been demonstrated that CNT yarns, made by twisting individual CNTs together, have outstanding repeatable and stable resistance–strain behaviors. Yarn arrays can be permanently integrated within a composite structure conveniently during fabrication with minimal invasiveness and weight punishment. The embedded yarn sensors can be used to monitor the initiation and propagation of cracks in composite structures in real time, as well as to work as a general strain gauge if top-mounted on the structural components.

Acknowledgments

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