A piezoresistive sensor based on carbon nanotube yarns

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Abstract

This work introduces macroscopic yarns made up of carbon nanotubes (CNT) as piezoresistive sensors for structural health monitoring (SHM). When highly crystalline and of few layers, carbon nanotubes combine exceptional mechanical and electrical properties with chemical resistance, large surface area and often a high aspect ratio (>10⁴). The “molecular” properties can be efficiently exploited by assembling CNT parallel to each other into a macroscopic, continuous fibre. We present mechanical properties of yarns made up of 10 to 100 filaments of 5 μm-thick CNT fibres. They have specific strength (0.46 GPa/SG) and toughness (33.7 J/g) above metals, mass-normalised conductivity approaching copper and very superior ductility to conventional glass (10.5% compared with <4%). We then show that CNT yarns are piezoresistive, with changes in electrical resistance correlating with longitudinal stress, rather than strain. From measurements on different fibre grades and lengths we extract a figure of merit for piezoresistance, equivalent to a gauge factor. A typical yarn undergoes a 10% change in longitudinal resistance for a 0.2 GPa/SG axial stress. Cyclic tests are also presented to discriminate between elastic and plastic piezoresistive effects.

1. INTRODUCTION

Soon after the identification in 1991 by Sumio Lijima [1], CNTs have shown enormous potential for sensing related applications. Their combination of high carrier mobility and a low carrier density (near the Fermi level) makes them sensitive to the presence of adsorbed molecules, electrochemical potential, or mechanical stresses that break the CNT symmetry. Experimental examples include exposure to different gases (ammonia, NO₂, etc) [2] and piezoresistive measurements upon mechanical deformation of individual CNTs [3]. These effects are more pronounced in CNTs with a high degree of
perfection and a small number of layers that thus preserve low-dimensional properties, such as the various features in the density of states, ballistic transport and quantized conductance. A review of chemo and piezoresistive mechanisms in single-walled can be found elsewhere.[4]

However, nanotubes present diameter sizes in the range 1-100nm and lengths up to millimeters [5], suitable for small sensing, for example field-effect transistors, but too small for large area detection. In order to use them for structural health monitoring applications two main routes have been put forward.

The first consists in dispersing CNTs in a polymeric matrix at low concentrations but above electrical percolation (0.01 -1 vol.%). The resulting network has electrical properties dominated by inter-tube charge transfer, often mediated by the polymer. It is thus sensitive to matrix deformation that can change the average CNT separation and orientation. Although popular because of its simplicity, this method has found limited application due to the difficulty in achieving reproducible and stable network structures. The signal extracted from the percolating material is also often non-linear and very sensitive to temperature.

Another strategy to exploit the sensing properties of CNTs consists in producing continuous macroscopic fibres made up of CNTs. An example of such material is presented in Figure 1 for a macroscopic yarn consists of various 5-micron thick CNT fibre filaments. The filaments are themselves made up of bundles of CNTs, which are imperfectly packed and thus give rise to a large porosity. Because of their piezoresistive properties [6], the yarns that can be embedded in composite structures or other materials for their use as sensors [7]. For example, CNT fibres have been successfully integrated in glass fibre laminates for SHM applications [8].

Amongst CNT fibre fabrication methods, the direct spinning method has proven particularly promising for large scale production of highly graphitised fibres. It is based on directly drawing and aerogel from the gas phase during chemical vapour deposition synthesis of CNTs Li et al [9]. Fibres made up of highly aligned few-layer CNTs can be currently produced at fast rates (40m/min) on a 10’s km per day scale in the laboratory using such method [10]. This work presents mechanical and piezoresistive properties of yarns consisting of 10 to 100 filaments of these CNT fibres. We study the behavior of CNT fibres under static and cyclic loads and propose gauge factors for sensitivity and repeatability of such sensors.
Figure 1: Hierachical structure showed by a CNT fibre: CNTs are packed into bundles entangled into an anisotropic network (right) leading to a macroscopic fibre (left). [9]

DESCRIPTION OF METHODS

2.1. Preparation of the samples

Samples of as-spun CNT fiber used in this work were all produced in the Multifunctional Nanocomposites Group at IMDEA Materials Institute using the direct spinning method. This technique is based on the formation of a CNT aerogel in the CVD reaction zone of a vertical furnace from which it can be mechanically drawn and wound onto a rotating spool as shown in Figure 2. The reaction consists in the growth of nanotubes from the decomposition of carbon sources at a high temperature (1250°C) in the presence of a group-16 element promoter (e.g. sulphur) and an iron catalyst in a reducing hydrogen atmosphere. The reaction was carried out using a precursor (carbon source, ferrocene, thiphene) feed rate of 2.5 mL/h and a winding rate of 10-30 m/min. Yarns of multiple filaments were produced by manual by consolidation of as-spun material and subsequently densified via capillary infiltration of acetone.
2.2. Piezoresistance measurements

2.2.1 Mechanical tests

To carry out tensile tests, FAVIMAT+ was used. As it is shown in Figure 3, the machine consists basically on two grips to hold the fibre and a device to develop linear density measurements. Thus, the fibre was placed between both grips with a small peg hanging to it in order to stretch the fibre. Once the grips were closed, the fibre was submitted to a pretension of 1cN/tex to avoid any possible compressive stress. The linear density was measured by a vibrational method which determines the fiber’s resonance frequency. Hence, taking into account the gauge length (30mm), it is easily deduced the linear density measured in tex=g*km\(^{-1}\).
Figure 3: Picture of the set-up developed for piezoresistance measurements of the fibre

In order to study both the gauge factor and the repeatability of the fibre two different tests were developed:

- Tensile test up to breackage. In this test, the fibre is submitted to a constant elongation speed of 1mm/min while the force exerted by this is monitored. The test end when the force drops a 90% or more.

- Cyclic tests. A cycle is defined as the process in which the fibre is elongated until a maximum strain to be restored to its original position. The parameters fixed during this experiments were the maximum strain (2%) and the strain rate (1mm/min). Finally the fibre was submitted to 10 cycles before the experiment finished.

2.2.2 Electrical measurements

The electrical contacts were made of aluminum foil and placed around the FAVIMAT+ grips, as shown in Figure 3. DC electrical resistance was monitored using an Agilent U1253B True RMS OLED multimeter.
3. RESULTS AND DISCUSSION

3.1 Tensile test up to breakage

![Figure 4: Stress-strain curves obtained from 3 CNT fibre samples](image)

The starting point of this work is the tensile test of the CNT yarns used in this study. Figure 4 shows 3 different stress-strain curves corresponding to 3 different samples. In all of them a good qualitative and quantitative correspondence can be seen, ensuring sample reproducibility. In fact, all the threads tested show practically the same elastoplastic behavior. According to the graph, there is an elastic region until ~2% of strain followed by a region in which the fibre seems to deform plastically until its final breakage. From these graphs the elastic modulus, tensile strength, strain-to-break are extracted. Stress (yield strength) and strain (yield strain) values at the point of pseudoyield were determined from the inflection point of the curves. All the values obtained from the analysis of Figure 4 are included in Table 1.

Table 1: Parameters obtained from tensile test of CNT fibre yarns.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Elastic modulus (GPa/SG)</th>
<th>Ultimate strength (GPa/SG)</th>
<th>Ultimate strain (%)</th>
<th>Yield strength (GPa/SG)</th>
<th>Yield strain (%)</th>
<th>$\varepsilon_{res}$ (%)</th>
<th>$\sigma_{res}$ (GPa/SG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.5</td>
<td>0.45</td>
<td>10.00</td>
<td>0.25</td>
<td>3.27</td>
<td>2.38</td>
<td>0.20</td>
</tr>
<tr>
<td>2</td>
<td>8.4</td>
<td>0.45</td>
<td>10.53</td>
<td>0.22</td>
<td>2.97</td>
<td>2.82</td>
<td>0.21</td>
</tr>
<tr>
<td>3</td>
<td>8.9</td>
<td>0.47</td>
<td>10.93</td>
<td>0.22</td>
<td>2.82</td>
<td>2.12</td>
<td>0.17</td>
</tr>
</tbody>
</table>
Once the mechanical behavior has been analyzed, Figure 5a shows the increase of relative resistance against the strain for the three samples previously presented. A first view indicates an almost identical shape of the three curves with two linear regions clearly differentiated. Thus, the relative resistance increases at a constant rate up to a determined strain from which it grows slower. This turning point is determined as the cut-off point of the two linear fittings corresponding to each linear region (Figure 5b). The change in slope in the resistance plot occurs at a strain, $\varepsilon_{res}$, that closely matches the yield point (Table 1). This result is in contrast with various strain gauges, including CNT-based networks, whose piezoresponse derives from resistance changes associated with volumetric strains.

**Figure 5:** Piezoresistive measurements on CNT fibre yarns. a) Relative resistance of three CNT yarn samples against their strain during the tensile test. b) Schematic of the method used to evaluate the pseudo yield points ($\varepsilon_0$, $\sigma_0$). c) Relative resistance now plotted against fibre axial stress.

When the electrical response is plotted against the longitudinal stress during tensile deformation, the correlation between the two becomes apparent. The relative resistance
plotted against the stress (Figure 5c) shows that the linear response remains from the beginning of the test up to fibre fracture. This result is consistent with recent results obtained on individual CNT fibres filaments produced using the same method [6].

From Figure 5c, it is also evident that the slope of the curve is related to the gauge factor of the CNT yarns. Next, we take the value of the slope for each sensor used in this work and plot it against the initial resistance of each sample (Figure 6). The use of yarns of different thickness results in different values of gauge factor \((\Delta R/R_0)/\sigma\) but which fall on the same line. This behavior is expected and simply reflects the fact that the sensor operates through changes in resistivity but with the output signal determined by geometrical parameters of the sample (i.e. through resistance). Moreover, the linear fitting crossing nearly through the origin confirms that the effect of electrical contacts is negligible. From a practical standpoint the implication is that the piezoresistance of the yarns has linear dependence on most parameters, which is often sought in SHM applications. As figures of merit for piezoresistive sensing, we calculate values of: i) 6% relative resistance change per 0.1 GPa/SG stress and ii) 6.5 Ω absolute change in resistance per 10 cN load for a 40 μm-thick sensor.

**Figure 6:** Linear relationship between the gauge factor of different samples against their initial resistance.

### 3.2. Cyclic tests

Finally, we study the piezoresistance of CNT yarns under cyclic loading. Figure 7a presents an example of stress-strain curves for 10 cycles a tensile deformation. The test corresponds to cyclic deformation to 2% nominal strain, a deformation still below the pseudoyield point. The curves show plastic deformation, load-unload hysteresis and “strain hardening”. After the first load-unload cycle the modulus of the sample increases by 33%, as shown in Figure 7b for the first two cycles.
The electrical response of fibres during the cyclic loading test in Figure 7 was also monitored. As Figure 8a shows, there is good correspondence in time between the peaks shown by both signals. It implies a rapid of the piezoresistive mechanism. With respect to the gradual increment in initial resistance before each cycle, we note that the graph in Figure 8a corresponds to changes in resistance with respect to the nominal initial resistance $R_0$. However, because of plastic deformation after each cycle, it is clear that the initial resistance will increase slightly. When this effect is taken into account, the gauge factor of the yarn is observed to be nearly constant throughout the cycles (Figure 8b), save for the initial increase due to the “strain-hardening” effect discussed above.

4. CONCLUSION

This work presents a piezoresistive study of macroscopic yarns made up of CNTs as a step towards their use in structural health monitoring of composites. The CNT yarns are
shown to have density-normalised tensile properties superior to those of metals, with ductility and toughness above glass.

Piezoresistive measurements show a linear increase in longitudinal electrical resistance with applied tensile stress. This effect is in contrast with conventional strain gauges, including networks of nanocarbons, and points to the inherent piezoresistance of the constituent CNTs as the origin of the bulk effect observed. Experiments are in progress to clarify this mechanism.

The slope of relative resistance change versus applied stress is taken as a gauge factor and a figure of merit for piezoresistive sensing. This parameter depends on yarn thickness, as expected for a mechanism involving changes that scale with sample cross-section. Comparison of sensors of different thickness shows good reproducibility between samples.

Cyclic load-unload samples showed a rapid piezoresistive response. The small changes in initial resistance after each cycle can be rationalised in terms of the elastoplastic response of the fibres and strain-hardening in the first cycles.

Future work should address the implementation of CNT fibres in composites and the study of piezoresistive properties embedded in a polymer matrix. An immediate challenge consists in developing strategies for integration in conductive fibre composites, for example containing carbon fibres, whilst avoiding short circuits.

REFERENCES

