Mechanics of a Carbon Nanocoil

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ABSTRACT

An individual carbon nanocoil was clamped between two AFM cantilevers and loaded in tension to a maximum relative elongation of ~42%. The deformation of the nanocoil agrees well with an analytical model of the spring constant that accounts for the geometric nonlinearity. The nanocoil behaves like an elastic spring with a spring constant $K$ of 0.12 N/m in the low strain region. No plastic deformation was detected. High-resolution microscopy images and the electron energy loss spectrum (EELS) indicate that the nanocoils are amorphous with a $sp^2/sp^3$ bonded-carbon ratio of ~4:1.

Carbon micro- and nanocoils have been synthesized and studied.1–6 Because of their unique 3D structure, they have potential applications as mechanical components such as resonating elements and nanosprings or as a novel reinforcement in high-strain composites. Other potential applications are as nanosolenoids and electromagnetic wave absorbers. Volodin et al.7 reported the elastic properties of coiled carbon nanotubes as measured with force modulation microscopy (an AFM technique). The tensile properties of helical diamond microfibers several millimeters in length and having a wire core of platinum have been discussed.8 Nakayama et al.9 presented a brief report on the mechanical properties of carbon nanocoils, and Motojima et al.10 described the mechanical response of carbon microcoils under extension. Amorphous helical SiO$_2$ nanosprings have also been recently characterized by scanning and transmission electron microscopy and atomic force microscopy11. However, a direct experimental measurement of the mechanical response of carbon nanocoils under tensile loading has not yet been conducted and is the focus of the present study.

This carbon nanocoil was studied using a home-built nanomanipulator tool operated inside of a scanning electron microscope (SEM, LEO 1525). The nanocoil was picked up and then clamped between two AFM cantilever tips with the electron beam-induced deposition (EBID) method. A stiff AFM cantilever (chip NSC12; we used the longest of the six cantilevers on the chip with a spring constant of $k$ 0.1 to 0.4 N/m provided by Mikromasch) is attached to one end of the nanocoil. The deformation of the compliant AFM cantilever (chip CSC12; we again used the longest cantilever on the chip, with $k$ 0.01 to 0.08 N/m as quoted by the manufacturer) is used as a force-sensing element. The applied force is calculated from the observed deflection of the soft cantilever, and the nanocoil elongation is determined from the acquired SEM images.

For the tensile loading experiment, two ultrasharp AFM cantilevers from Mikromasch, Inc. were mounted on the nanomanipulator. A stiff AFM cantilever (chip NSC12; we used the longest of the six cantilevers on the chip with a spring constant of $k$ ~0.1 to 0.4 N/m provided by Mikromasch) is attached to one end of the nanocoil. The deformation of the compliant AFM cantilever (chip CSC12; we again used the longest cantilever on the chip, with $k$ ~0.01 to 0.08 N/m as quoted by the manufacturer) is used as a force-sensing element. The applied force is calculated from the observed deflection of the soft cantilever, and the nanocoil elongation is determined from the acquired SEM images.

A typical mounting operation involves approaching an individual nanocoil with the rigid cantilever tip and then...
creating a clamp on the tip by EBID of residual hydrocarbons in the SEM environment. The desire to extract an individual nanocoil for subsequent mounting onto the opposing cantilever tip was typically thwarted because of the extension of the nanocoil to a certain point, followed by violent detachment that often resulted in the loss of the nanocoil because of its having "sprung away." The nanocoil that is the subject of this paper was actually first studied by extending it with respect to the source (the tape on the metal wire). We were fortunate to succeed in freeing it from the substrate at an elongation of ~42%, as measured by the relative displacement between six turns in the nanocoil as shown in Figure 2, without the clamp failing at the tip. We note that this carbon nanocoil returned completely to its relaxed geometry after loading without apparent plastic deformation.

Once the nanocoil was freed from the source as described above, the more compliant cantilever tip was brought into contact with the opposite end of the nanocoil and attached via another EBID clamp. The nanocoil was then subject to tensile loading by applying a series of discrete voltages to a piezoelectric multilayer bender (Noliac A/S, Denmark, ceramic multilayer bender B1) as shown in Figure 3, where the cantilever on the left is the stiffer cantilever and the one on the right is the more compliant cantilever. The displacement of the more compliant cantilever, with a spring constant of $k = 0.047 \pm 0.003$ N/m, was used to measure the applied load. (We discuss the calibration of the AFM cantilevers below.) Also shown in Figure 3 are images of the nanocoil at 20% and 33% relative elongation. After reaching the maximum 33% relative elongation, the load was slowly released, and the nanocoil relaxed to its original length and geometry. Again, no plastic deformation was identified after the nanocoil was unloaded.

Previously, a method that we use for measuring small (ranging from fractions of a micro-Newton to micro-Newton) applied forces from small cantilever deflections has been described. The displacement of the relatively soft cantilever AFM tip was calibrated as a function of the voltage applied to the piezoelectric bender. The displacement of the tip both with and without the nanocoil was measured with the same potential (volts) applied to the piezoelectric bender. The difference between the two displacements is the true deflection of the AFM cantilever. This method allows accurate measurements of small displacements by tracking the AFM tip position at the highest SEM magnification.

Figure 1. (a) SEM image of carbon nanocoils. (b) Schematic of tensile loading of an individual nanocoil.

Figure 2. (a) Nanocoil picked up by the AFM tip. (b) Nanocoil extension upon extraction from the substrate. (c) Nanocoil detachment from the substrate. The distance between the six turns is, within experimental error, identical to the equivalent distance in (a).

Figure 3. (a) Nanocoil clamped between two AFM cantilevers. The left cantilever is stiffer than the right cantilever. (b) Relaxed nanocoil prior to loading. (c) Nanocoil at a relative elongation of 20%. (d) Nanocoil at a relative elongation of 33%.

The spring constant of each cantilever was calibrated before the tensile loading experiment. The calibration procedure is based on the method reported in ref 15. The resonance frequency of each cantilever and all of the
The resonance frequency in vacuum (\(\omega_{\text{vac}}\)) of the cantilever as measured in the SEM was 15 kHz and by setting \(\omega_{\text{vac}} = 2\pi f_{\text{vac}}\), the geom-etry of the soft cantilever and shear modulus of the material can be determined by using the principle of virtual work: 18

\[
\Delta = \int_0^l N_s \frac{Q_s}{EA} \, ds + \int_0^l \frac{\alpha_s Q_s Q_F}{AG} \, ds + \int_0^l \frac{M_s M_F}{EI} \, ds + \int_0^l \frac{T_s T_F}{GJ} \, ds
\]  

where \(l\) is the total length of the unit cell, \(\alpha_s\) is the shear coefficient, \(E\) is the tensile modulus, \(A\) is the cross-sectional area of the coil wire, \(I\) is the moment of inertia, and \(J\) is the polar moment of inertia of the cross section. The variables \(N_s, Q_s, M_s\), and \(T_s\) are the axial force, shear force, bending moment, and torsion, respectively, caused by a unit tensile load of \(P_s = 1\) along the axial direction. \(N_F, Q_F, M_F,\) and \(T_F\) are the tension, shear, bending moment, and torsion, respectively, caused by the applied tensile force \(F\).

An arbitrary point along the central line of the unit cell has spatial coordinates of \([R \cos \theta, R \sin \theta, (h/2\pi)\theta]\), where \(\theta\) is the radial angle ranging from 0 to \(2\pi\) and \(h\) the height of the unit cell. The tangential direction at this point is then \((-R \sin \theta, R \cos \theta, h/2\pi)\). The length of unit cell is thus \(l = 2\pi \sqrt{R^2 + H^2}\), where \(H = h/2\pi\). We assume that \(l\) is constant. Denoting \(\varphi\) as the angle between the tangential direction and the axial direction of the coil gives \(\cos \varphi = \)}
where the unit coil is extended as 

\[ \text{tension: } N_F = F \cdot \cos \varphi = \frac{FH}{\sqrt{R^2 + H^2}} \]

\[ \text{shear: } Q_F = F \cdot \sin \varphi = \frac{FR}{\sqrt{R^2 + H^2}} \]

\[ \text{bending: } M_F = F \cdot \cos \varphi \cdot R = \frac{FRH}{\sqrt{R^2 + H^2}} \]

\[ \text{torsion: } T_F = F \cdot \sin \varphi \cdot R = \frac{FR^2}{\sqrt{R^2 + H^2}} \]

Then, eq 2 can be rewritten as follows:

\[ \Delta = \frac{FH^2}{R^2 + H^2} \cdot \frac{l}{EA} + \frac{FR^2}{R^2 + H^2} \cdot \frac{l}{GA} + \frac{FR^2H^2}{R^2 + H^2} \cdot \frac{l}{EI} + \frac{FR^4}{R^2 + H^2} \cdot \frac{l}{GJ} \] (3)

We define \( K = F/\Delta \) such that

\[ \frac{1}{K} = \frac{H^2}{R^2 + H^2} \cdot \frac{l}{EA} + \frac{\alpha_r R^2}{R^2 + H^2} \cdot \frac{l}{GA} + \frac{R^2H^2}{R^2 + H^2} \cdot \frac{l}{EI} + \frac{R^4}{R^2 + H^2} \cdot \frac{l}{GJ} \] (4)

where \( \alpha_r = (7 + 6\nu)/(1 + \nu) \) and \( \nu \) is Poisson’s ratio. If the unit coil is extended as \( \Delta \), then \( H = (h + \Delta)/2\pi \) and \( R = \sqrt{(R^2 - (h + \Delta)^2)/(2\pi)^2} \).

For a coil wire of circular cross section,

\[ A = \frac{\pi d^2}{4} \quad I = \frac{\pi d^4}{64} \quad J = \frac{\pi d^4}{32} \]

By substituting the above expressions into eq 4, one has

\[ \frac{1}{K} = \frac{8H^2}{Ed^2 \sqrt{R^2 + H^2}} + \frac{8\alpha_r R^2}{Gd^2 \sqrt{R^2 + H^2}} + \frac{128R^2H^2}{Ed^2 \sqrt{R^2 + H^2}} + \frac{64R^4}{Gd^2 \sqrt{R^2 + H^2}} \] (5)

where \( E = 2(1 + \nu)G \). We define \( \beta = 2(1 + \nu) \). Then,

\[ K = \frac{Gd^4}{64R^3} \frac{1}{\xi} \] (6)

where \( \xi \) is a dimensionless coefficient that describes the geometry of the coil,

\[ \xi = \frac{H^2d^2}{8\beta R^4 \sqrt{R^2 + H^2}} + \frac{\alpha_r d^2}{8R \sqrt{R^2 + H^2}} + \frac{2H^2}{\beta R \sqrt{R^2 + H^2}} + \frac{R}{\sqrt{R^2 + H^2}} \] (7)

For coil springs that are composed of \( N \) turns, eq 6 can be rewritten as

\[ K = \frac{Gd^4}{64R^3} \frac{1}{\xi} \] (8)

For a coiled nanotube with outer diameter \( d_1 \) and inner diameter \( d_2 \), eq 8 can be rewritten as

\[ K = \frac{G(d_1^4 - d_2^4)}{64R^3} \frac{1}{\xi} \] (9)

where \( \xi \) is expressed as:

\[ \xi = \frac{H^2(d_1^2 + d_2^2)}{8\beta R^4 \sqrt{R^2 + H^2}} + \frac{\alpha_r (d_1^2 + d_2^2)}{8R \sqrt{R^2 + H^2}} + \frac{2H^2}{\beta R \sqrt{R^2 + H^2}} + \frac{R}{\sqrt{R^2 + H^2}} \] (10)

Equations 8 and 9 take into account the nonlinear relationship between the shear modulus and the set of measured spring constants. Hence, it is valid as long as the deformation of the coil spring remains in the elastic regime. In the limiting case \( R \gg H \), the first three terms on the right side of eq 7 are negligible compared with the fourth term, leading to the simplified case described by eq 1. However, if \( R \ll H \), then eq 8 is reduced to the case of uniaxial elongation of a straight beam.

We consider two examples to discuss the above analysis. The first example is a unit nanocoil with \( d = 120 \text{ nm}, R = 420 \text{ nm}, h = 120 \text{ nm}, G = 2.5 \text{ GPa}, \nu = 0.27 \), and a very small helical angle. Figure 6a plots the spring constant versus relative elongation based on eq 6. It indicates that the spring constant remains constant even though the relative elongation exceeds 30%. Figure 6b shows the contribution to the spring constant from the tension, bending, shear, and torsion generated by the extension of the coil based on eq 7. It clearly shows that torsion dominates the response and that the contributions from the tension, bending, and shear components are negligible. For the second example, we consider a nanocoil with a larger helical angle for which \( h = 2000 \text{ nm} \) and the rest of the parameters are the same as in the first case. Parts c and d of Figure 6 show the plot of the spring constant versus relative elongation and the percentage contribution to the spring constant from the tension, bending, shear, and torsion generated by the extension of the coil. The results show that the spring constant will increase as
the coil is extended even though the relative elongation is less than 30%. In this case, both the bending and the torsion contribute significantly to the response. The bending contribution increases and the torsion contribution decreases with increasing relative elongation.

The experimental nanocoil behavior discussed earlier is similar to the second example. According to eq 8, as the nanocoil is elongated under pure tensile load, the coil radius $R$ decreases, and the spring constant increases because the other variables such as coil wire diameter $d$ and shear modulus $G$ are assumed to be constant in this analysis. From the comparison between Figures 4c and 6c, it is clear that the experimental data are consistent with this theoretical analysis.

The growth mechanism of carbon nanocoils has been discussed in the literature. The catalyst is located at the tip of the nanocoil, indicating a tip-growth mechanism. The TEM diffraction pattern shown in the inset of Figure 7a was taken using another carbon nanocoil and demonstrates that it is amorphous. As shown in Figure 7, SEM and TEM images indicate that most of the nanocoils consist of more than one wire and typically have a double-helical structure. In addition, the TEM image in Figure 7a shows that each wire of the nanocoil is hollow.

Figure 7b shows a relatively high magnification SEM image of the nanocoil that was mechanically loaded, and the inset of Figure 7b shows a schematic of a double coil. As mentioned above, this nanocoil was stretched several times, and even though the relative elongation reached 42%, no separation or sliding between the two wires was observed. This suggests that the two wires are tightly joined. Thus, for purposes of modeling, we assume that the cross section of the nanocoil is two joined tubes. The outer diameter (o.d.) of each tube is $\sim 126 \pm 4$ nm, as measured from the SEM image. Although the inner diameter (i.d.) of this particular nanocoil is unknown, below we consider a few different cases. If the i.d. = $3/4$ that of the o.d., then the shear modulus $G$ fitted according to eq 4 is $\sim 2.5 \pm 0.4$ GPa, which is the mean value of the 21 $G$ values fit to the 21 measured ($K$, elongation) points. If i.d. = 1/2 o.d., then the mean value of $G$ is $\sim 2.3 \pm 0.4$ GPa, and for two joined (solid) wires (i.d. = 0), the mean value of $G$ will be $\sim 2.1 \pm 0.3$ GPa. Thus, the value of $G$ does not depend very strongly on the inner diameter of the individual tubes. These results indicate that the shear modulus $G$ of the carbon nanocoil is much lower than that of carbon nanotubes for which a shear modulus of roughly 400 GPa has been estimated. A future area of study...
is the graphitization of the carbon nanocoils to enhance their mechanical properties.

The electron energy loss spectrum (EELS) of the carbon nanocoils was obtained with a Hitachi HF2000 at 200 keV as shown in Figure 7c. Carbon was the only element detected in the nanocoil. (It is difficult to detect hydrogen with EELS.) To get the sp²/sp³ ratio of the nanocoil sample, a graphite sample was used as a reference for pure sp² bonding. The graphite sample was prepared by cleaving fragments from a bulk specimen of highly oriented pyrolytic graphite (HOPG). The HOPG fragments were ground into fine powder using a mortar and pestle and dispersed in acetone. One drop of this suspension was put on a lacey carbon grid so that after drying many graphite platelets were attached to the grid. Because the graphite is anisotropic, the observed intensity depends on the orientation of the beam with respect to the graphite layer; here the spectrum was recorded with the beam parallel to the graphite layer. EELS data were taken in parallel with the graphite layer; here the spectrum was recorded with the beam inside of a scanning electron microscope. The nanocoil were characterized on the basis of a nonlinear mechanical properties. The mechanical properties of the nanocoil was obtained with a Hitachi HF2000 at 200 keV and characterized by transmission electron microscopy images and diffraction patterns and the shear modulus $G$ in which the contributions of all of the components of the restoring force are included. Several nanocoils in the sample were characterized by transmission electron microscopy images and diffraction patterns and electron energy loss spectroscopy. The results indicate that the nanocoils are double- (and even in some cases triple-) coiled amorphous carbon nanotubes having a relatively high sp² bonding content.

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