

Fatigue resistance of aligned carbon nanotube arrays under cyclic compression

J. SUHR^{1*}†, P. VICTOR^{2*}, L. CI², S. SREEKALA³, X. ZHANG⁴, O. NALAMASU² AND P. M. AJAYAN^{2†}

¹Department of Mechanical Engineering, The University of Nevada, Reno, Nevada 89557, USA

²Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York 12180, USA

³Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey 08540, USA

⁴School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200030, China

*These authors contributed equally to this work.

†e-mail: ajayan@rpi.edu; suhrjh@unr.edu

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Structural components subject to cyclic stress can succumb to fatigue, causing them to fail at stress levels much lower than if they were under static mechanical loading¹. However, despite extensive research into the mechanical properties of carbon nanotube structures^{2–9} for more than a decade, data on the fatigue behaviour of such devices have never been reported. We show that under repeated high compressive strains, long, vertically aligned multiwalled nanotubes exhibit viscoelastic behaviour similar to that observed in soft-tissue membranes^{10,11}. Under compressive cyclic loading, the mechanical response of the nanotube arrays shows preconditioning, characteristic viscoelasticity-induced hysteresis, nonlinear elasticity and stress relaxation, and large deformations. Furthermore, no fatigue failure is observed at high strain amplitudes up to half a million cycles. This combination of soft-tissue-like behaviour and outstanding fatigue resistance suggests that properly engineered nanotube structures could mimic artificial tissues, and that their good electrical conductivity could lead to their use as compliant electrical contacts in a variety of applications.

Blocks of vertically aligned multiwalled carbon nanotubes (CNTs) (Fig. 1a) were made using chemical vapour deposition (CVD; see Methods). The CNT blocks have very low density (<10%) and the nanotubes (average diameter of ~50 nm) are held together by van der Waals forces. The nanotube blocks were tested under compressive cyclic loading (loading–unloading) as illustrated in Fig. 1b. Figure 1a shows a scanning electron microscope (SEM) image of the nanotube array before testing (see Methods for the structural details of the nanotube block).

The stress responses (Fig. 1c) were measured at a constant compressive strain level (15%) as a function of the number of cycles. A transient phenomenon in stress response can be observed. During the initial cycles, the stress response was measured to be up to ~0.73 MPa, but subsequent cycles (after 60 cycles) show that the induced stress response has gradually decreased and become stationary, reaching a constant stress amplitude (~0.58 MPa). This indicates a stress softening, which is often observed in soft-tissue materials^{10,11}, where such behaviour is called ‘preconditioning’. The induced stress versus applied strain curves (Fig. 2a) clearly show two distinct paths corresponding to the loading and unloading trajectories, generating hysteresis loops. The area of the hysteresis loop is larger during the first several

cycles, becoming smaller for the subsequent cycles. Eventually, the loading and unloading paths reach a steady state, displaying a shape memory characteristic along a given loading path.

The preconditioning may arise from the collective behaviour of the nanotubes in the block (tube–tube interactions such as disentanglements, similar to polymer chains, relocation and reordering, and so on). The cyclic loading in compression breaks the long-range van der Waals interactions existing between the nanotubes in the initial cycles, and then equilibrium conditions are reached at the imposed loading condition for the subsequent cycles. In addition, it has recently been observed¹³ that axial compression produces kinks and defects that are not lost during unloading. Some of these stress-generated kinks and defects existing on any nanotube during any of the cycles could persist and affect the stress-softening behaviour observed after many cycles.

Similar to the behaviour observed in polymer systems, hysteresis in the nanotube arrays during compressive cycles could result from changes in the orientation or waviness of individual nanotubes during loading–unloading cycles. For instance, when nanotubes in the block are compressed, the vertically aligned individual nanotubes become much more wavy and less oriented, requiring the nanotubes to absorb thermal energy from their surroundings. In contrast, on release of loading, nanotubes recover their alignment and orientation while dissipating thermal energy. This heat transfer between the nanotubes and their surroundings (including dissipation of frictional energy between adjacent nanotubes¹⁴) can generate two distinct loading paths, forming a hysteresis loop (Fig. 2a). The observations of preconditioning (stress level softening) and the hysteresis in the nanotube blocks suggest that the mechanical response of nanotube arrays in compression translates to viscoelastic behaviour. In fact, other evidence of viscoelastic properties is seen in the results from a static compression test, in which a monotonic compressive load was applied to the samples using the previously used test setup. When the samples are compressed and held at a certain strain level (or displacement), the induced stress gradually decreases over time. This suggests that the free-standing nanotube blocks show stress–relaxation behaviour, which proves their intrinsic viscoelasticity. Furthermore, the nanotube blocks exhibit nonlinear stress–strain

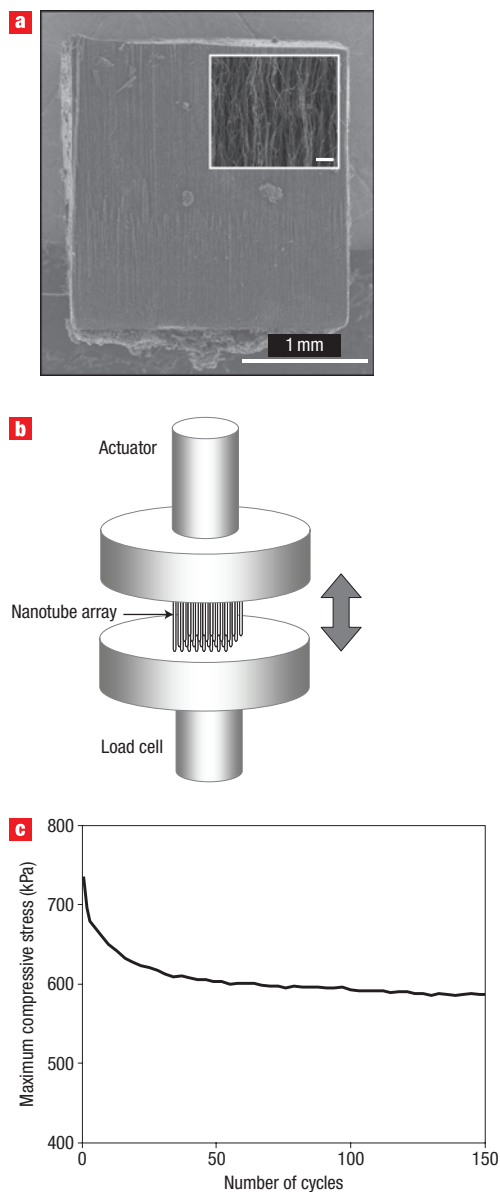


Figure 1 Compressive cyclic stress–strain characterization tests.

a, SEM image of the free-standing nanotube block before testing, showing the nanotubes' vertical alignment. The inset shows an SEM image of the nanotube block at high magnification (scale bar: 1 μm). The block consists of millions of vertically aligned multiwalled CNTs. The sample is ~ 2.2 mm in width, ~ 2.3 mm in length and ~ 2.2 mm in height. The density of the nanotube block is $< 10\%$. **b**, Schematic of compressive cyclic testing of vertically aligned CNT array blocks. Compression is made between two steel plates. **c**, Measured compressive stress response at a constant strain amplitude of 15% with respect to number of cycles. All tests are performed at a test frequency of 0.75 Hz. The preconditioning (stress-softening) behaviour is observed in the block's response under cyclic compressive loading and unloading.

behaviour under compressive strains of more than 60% (Fig. 2b), as previously reported⁷.

Figure 2b also shows that free-standing nanotube blocks exhibit a nonlinear stress–strain behaviour composed of two distinct modulus regions (low-modulus, or initial plateau, and high-modulus regimes). In the initial plateau region, as the nanotubes

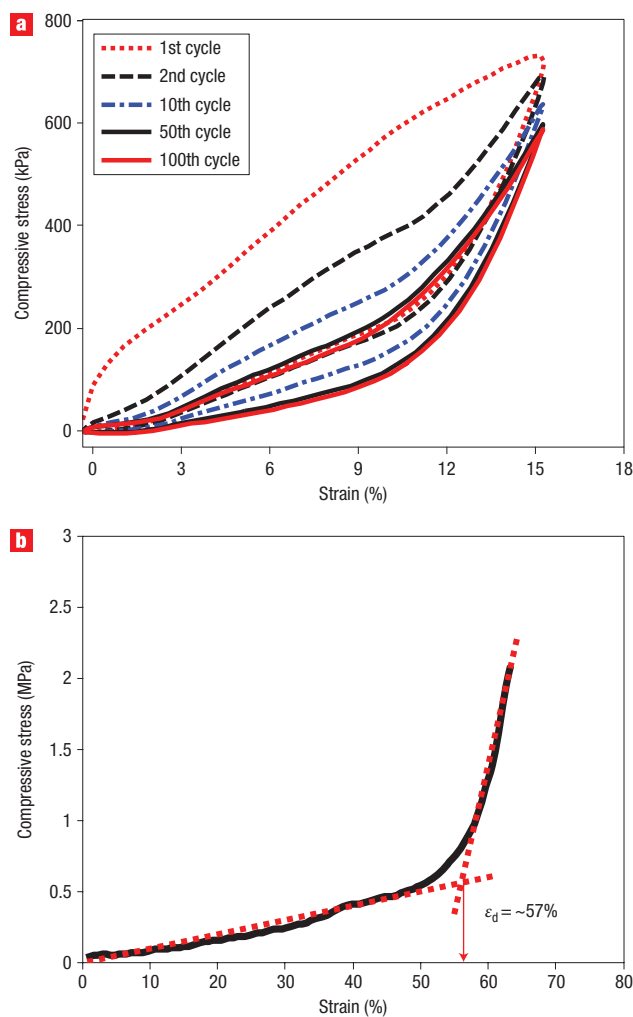


Figure 2 Hysteresis and nonlinear elastic behaviour of a multiwalled CNT block. **a**, Hysteresis stress–strain curves in compression. The area of the hysteresis loops decreases over the initial cycles and reaches equilibrium after a certain initial number of cycles. **b**, Monotonic stress–strain curve in compression showing nonlinear elasticity. Compressive strain is applied up to 63% and two distinct modulus regions are observed.

begin to resist the compressive load as strain increases, the stress gradually rises to 0.6 MPa, displaying a constant compressive modulus of the blocks (~ 1.0 MPa). The stress response then enters the maximum modulus region, showing a sharp increase to 2.1 MPa at $\sim 63\%$ strain, and the modulus of the sample approaches a maximum value of 20.8 MPa. This behaviour can be explained by comparison with open-cell foams¹⁵. The low-elastic region features progressively developing local buckling of individual nanotubes with increasing strain. Then, in contrast, as the nanotubes experience further compression, the collapse of individual nanotubes and densification of the nanotube structure results in rapid increase of the modulus. As shown in Fig. 2b, these regimes can be characterized by a critical strain, ε_d , of approximately 57%, defined by the intersection of the two asymptotic lines.

Here, the nanotube blocks exhibit compressibility as an ensemble, showing the collective behaviour of individual nanotubes buckling and recovering during cyclic loading. The

Table 1 Compressive properties and life cycles of some materials that exhibit stress and strain. Stress, strain, strain rate and life cycles for various contractile materials are compared, showing their peak values. These values are taken from several sources^{20–24}, except for those for the CNT arrays, which are obtained from the present study. The multiwalled CNT arrays are shown to be comparable to human muscle tissues in terms of mechanical properties.

Class	Subclass	Example	Stress level (MPa)	Strain (%)	Strain rate (s ⁻¹)	Life-cycles
Muscle	Skeletal	Human ²⁰	0.35	>40	5	>10 ⁹
Piezoelectric	Polymer	PVDF ^{21,22}	3	0.1	>1	>10 ⁶
Polymer	Conducting	Polyaniline ²³	180	>2	>1	>10 ⁵
Polymer	Gel	PVA–PAA ²⁴	0.3	>40	0.1	>10 ⁵
CNT arrays	Multiwalled	Carbon*	>2	>35	>0.75	>10 ⁶

*Data from present study.

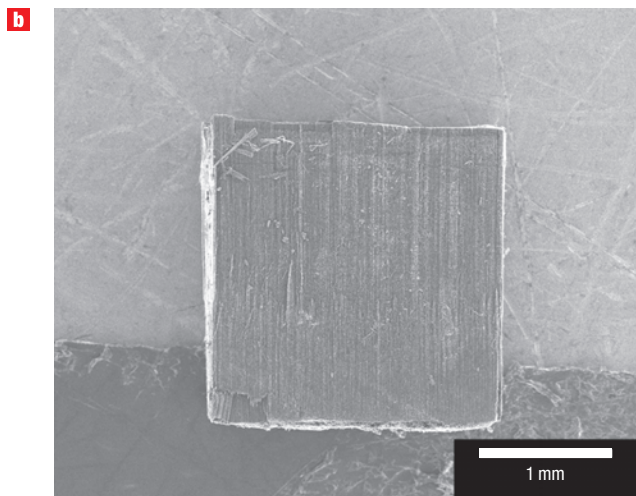
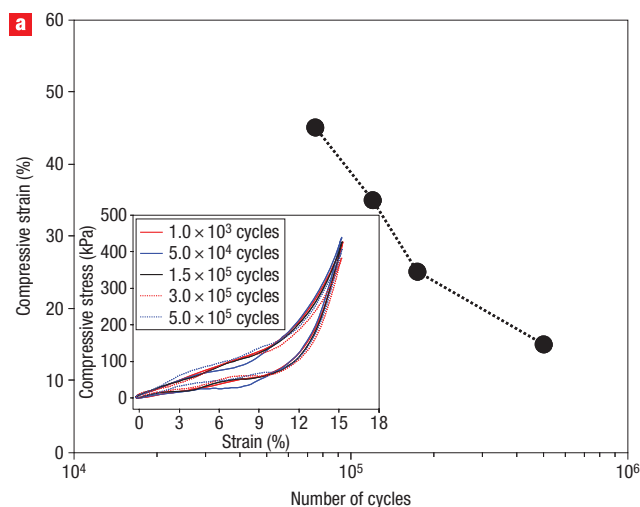


Figure 3 Strain–fatigue relation in cyclic strain controlled testing. **a**, Fatigue strain–life curve for the nanotube blocks. Tests are conducted over a strain amplitude range of 15 to ~45% in compression and at a test frequency of 0.75 Hz. All tests are performed at room temperature. No significant change of stress responses and hysteresis loops is shown for half a million cycles at 15% strain amplitude. **b**, SEM image of the nanotube block after fatigue testing. There is no significant structural damage even after half a million cycles at the strain amplitude of 15%. Note that less than 5% shrinkage along the height is observed.

volume change as the material is compressed is accommodated by the porosity in the arrays and so the sample as a whole does not undergo barrelling under compression. Interestingly, although the

individual nanotube behaviour is essentially elastic, the collective behaviour demonstrates a viscoelastic-like characteristic, as we have observed here.

Based on the above observations, it is noted that the free-standing nanotube arrays under compressive loading exhibit characteristics (preconditioning, hysteresis, nonlinear elasticity and stress relaxation) that are common features of viscoelastic materials. Also, the nanotube arrays undergo large elastic deformations. Soft-tissue materials have very similar mechanical properties^{10,11,16–18}, although they also show quasi-incompressible characteristics. Soft tissues also have fibrous structures made from hierarchical building-blocks¹⁸. For example, a tendon has a multilevel fibrous organization. These tendons are subject to cyclic loading, often undergoing large deformations up to strain levels of ~10% (ref. 18). It is expected that these have outstanding fatigue resistance because they need to withstand a large number of cycles during their lifetime. Another example is the stomach wall. Mechanically, the wall keeps expanding and contracting with certain strain amplitude and has to endure a large number of cycles over its lifetime. It is known¹⁹ that skeletal human muscle can deform at more than 40% strain, and can generate stress up to 0.35 MPa with an endurance of >10⁹ life cycles. Table 1 shows a comparison of the mechanical properties of CNT arrays and other materials, including skeletal muscle, under cyclic loading, and it is noted that the nanotube arrays compare well with the muscle tissue.

The preconditioned samples reached equilibrium in the stress–strain response before fatigue testing. In Fig. 3a the strain–life relationship is presented as a curve of strain versus fatigue life. At strain amplitudes of 25%, 35% and 45%, the alternating stress responses of the samples decrease appreciably after 1.75×10^5 , 1.2×10^5 and 7.5×10^4 cycles, respectively, suggesting that the nanotube arrays could degrade as a result of fatigue. Here fatigue failure is unlike what is typically seen in bulk materials. The fatigue that results in degradation could be the result of reconfiguration and orientational disorder of the collective nanotube array system, rather than fracture of individual nanotubes. At a strain level of 15%, the nanotube samples do not show any significant change in the stress responses or dimensional change in up to 0.5×10^6 (half a million) cycles (Fig. 3a, inset). This is the highest number of cycles for which we have carried out the loading tests, so it defines a lower limit of fatigue degradation in the arrays at 15% strain. The SEM image in Fig. 3b characterizes the structure of the nanotube array after fatigue testing (Fig. 1a shows the same sample before testing). The image confirms that at 15% strain level, the shrinkage is below the defined 10% fatigue damage (shrinkage) limit.

In addition to monitoring stability under long-time cyclic compression, the resistance of the nanotube arrays was measured (Fig. 4a) simultaneously under cyclic loading at a strain amplitude of ~25%. For applications in which the nanotube arrays are used as electrical contact brushes or flexible probes, the

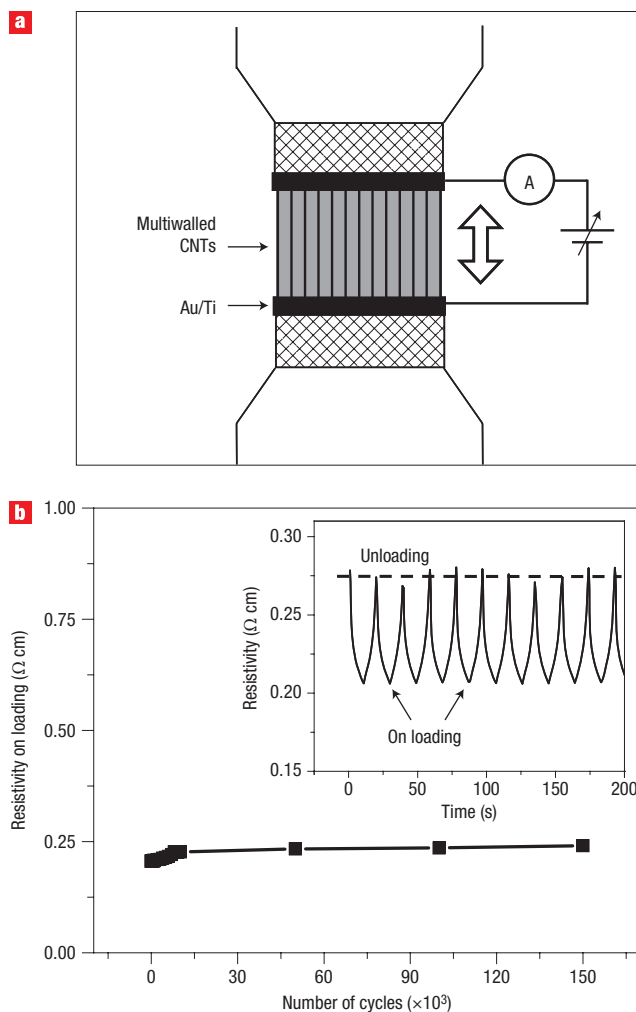


Figure 4 Electromechanical characterization test. **a**, Schematic diagram of the electromechanical tests carried out on the nanotube block. **b**, Resistivity of the CNT block under cyclic loading. The resistivity measured on the block was $\sim 0.25 \Omega \text{ cm}$ at a strain amplitude of 25%, showing minimal change ($\sim 5\%$ increase) after 1.5×10^5 cycles. The inset shows, at a specific strain (25%), the electrical response corresponding to the compressive cyclic loading.

challenge will be to create vertically aligned bundles of nanotubes that perform consistently over a large number of cycles. As shown in Fig. 4b, the original resistivity (first contact) was measured to be $\sim 0.25 \Omega \text{ cm}$, and showed minimal change (only 5% increase) after nearly 1.5×10^5 touchdown cycles. This indicates that such engineered nanotube architectures could survive the lifetime of electromechanical devices and survive, without any damage, over a very large number of contact cycles.

In conclusion, this study has shown that free-standing CNT arrays clearly exhibit viscoelastic behaviour under compression, and show no signs of fatigue under cyclic compressive loading up to very large numbers of cycles at relatively high strain levels. The behaviour is reminiscent of the mechanics of soft tissues under compression. The collective mechanical behaviour of nanotubes and the combination of their mechanical and electrical properties, as reported here, show potential for the use of engineered nanotube architectures in the building of synthetic biomaterials, contact probes or electromechanical devices in future applications.

METHODS

CNT GROWTH

The long multiwalled CNT array blocks were prepared by a xylene-ferrocene CVD method as reported previously¹². Typically, a xylene solution with a ferrocene concentration of 0.02 g ml^{-1} was used as the carbon and catalyst source. During the CVD process, a mixture of Ar and H_2 was blown through a reactor tube at a rate of 2,000/400 s.c.c.m. The xylene solution was fed continuously by a flux pump (at a feeding rate of 0.4 ml min^{-1}) to a preheating zone of 300°C , becoming vapour, and was then carried by the Ar/ H_2 gas into the 850°C growth zone. A high average CNT growth rate of $50 \mu\text{m min}^{-1}$ was achieved during growth, and CNT blocks several millimetres thick could be prepared easily in 1 to 4 h. The nanotube block samples tested in this study have a mean diameter of 53 nm, cross-sectional areas ranging from 1.5 to $\sim 3.0 \text{ mm}^2$, and are $\sim 2.5 \text{ mm}$ in height (along the nanotube length). The blocks of nanotubes used in the experiments are extended arrays of nanotubes grown on solid substrates and peeled off. These blocks are structures of very low density and are held together by van der Waals forces.

MECHANICAL TESTING (CYCLIC TESTING)

Figure 1b shows a schematic of the cyclic testing (loading–unloading) of an aligned nanotube block in compression. The nanotube blocks were tested using an Instron 5843 system at room temperature. All the tests were performed at a test frequency of 0.75 Hz. The nanotube blocks were cyclically compressed and released along their length at constant strain amplitude. While mounting the samples between the actuator and the load cell in the Instron, an initial loading of around 0.2 MPa was applied to the samples in order to provide uniform contact and also to prevent them from slipping. The applied compressive strain here was 15%, which was large enough to make individual nanotubes buckle. The compressive stress responses and applied strain amplitude were recorded using a load cell (10 N capacity) and a non-contact type video extensometer, respectively.

FATIGUE TESTING

The cyclic strain controlled loading was used to evaluate the fatigue behaviour of the nanotube arrays between 15% and 45% strain. The curve of strain versus the number of cycles to failure (strain–life curve) was used to examine fatigue resistance, as strain controlled cyclic testing was performed for all the samples. Note also that it is common to present a strain–life curve for characterization of low-cycle fatigue behaviour, for example in polymeric materials. In this study, in order to define qualitatively the fatigue life of the nanotube arrays, a perceptible decrease (15%) of the measured stress amplitude or more than 10% shrinkage from the original length was assumed to be a sign of fatigue failure (degradation). This is considered to be a metric that defines either an intrinsic property (stress-softening) change or a dimensional degradation (shrinkage) of the nanotube system.

ELECTRICAL TESTING

The vertically aligned multiwalled CNT arrays were sandwiched between the Ti/Au electrodes, and the electrical leads were taken out of the Ti/Au electrodes and connected to a Keithley 6430 source meter. A constant voltage ($\sim 100 \text{ mV}$) was used and the current was measured based on the strain applied to the nanotube arrays. Simultaneous electromechanical measurement was carried out, and the resistance was observed to drop on applying different levels of strain.

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Correspondence and request for materials should be addressed to P.M.A. and J.S.

Author contributions

All authors discussed the results and commented on the manuscript.

Competing financial interests

The authors declare no competing financial interests.

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