Tuning the compressive mechanical properties of carbon nanotube foam

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ABSTRACT

A post-growth chemical vapor deposition (CVD) treatment was used to tune the compressive mechanical properties of carbon nanotube (CNT) arrays. Millimeter tall CNT arrays with low compressive resilience were changed to a foam-like material with high compressive strength and almost complete recovery upon unloading. The foam was tuned to provide a range of compressive properties for various applications. The treated arrays demonstrated compressive strength up to 35 times greater than the as-grown CNT array. Unlike polymeric foams, the CNT foam did not decompose after exposure to high temperatures. Investigation of the foam structure revealed that the CVD treatment increased CNT diameter through radial growth, while increasing the CNT surface roughness. The morphological changes help to explain the increase in CNT array compressive strength and the transition from permanent array deformation to foam-like recovery after compressive loading.

1. Introduction

The combination of low density, high strength and high stiffness make carbon nanotube (CNT) structures attractive as multifunctional, high performance foam materials. Applications for CNT foams range from energy absorbing structures for acoustic, vibration, impact and shockwave mitigation [1], electromechanical devices based on compressibility and electrical response [2,3], compliant electrical contacts such as motor brushes [4] and lipophilic absorbent sponges [5]. Methods for producing CNT based foams include: growing random tangled networks of long CNTs in a chemical vapor deposition (CVD) furnace [5], foaming liquid or gel precursors loaded with CNTs and carbonizing the non-CNT material [6,7], and growing vertically aligned arrays of CNTs (also known as forests, mats, films brushes and turf) using CVD [8,9]. The first two approaches form a random network of CNTs, while CNT arrays are a porous network of aligned CNTs.

A vertically aligned CNT array acts as an assembly of strong struts or columns when a compressive force is applied parallel to the alignment direction. The compressive behavior of short CNT arrays (1–100 µm) has been studied with both indentation and impact testing, demonstrating high energy dissipation [10–15]. CNTs can be grown in aligned arrays to lengths of multiple millimeters through synthesis optimization [16–18]. The total energy absorption during compression or impact of millimeter tall CNT arrays is considerable. When CNT arrays are compressed, they have the tendency to permanently deform, allowing for little energy dissipation upon subsequent loading. Ideally, an energy absorbing CNT array would exhibit full recovery to its original dimensions after maximum compression. This desirable behavior has only

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been reported in a couple of instances for millimeter long arrays [1,2]. While the compressive properties of those arrays were thoroughly analyzed, the questions remain: (1) is it possible to tune the mechanical properties of the CNT array foam for a variety of practical applications? (2) what structural features are necessary for shape recovery in a CNT array foam?

2. Experimental

CNT arrays were produced through nano-particle catalyzed synthesis on a silicon wafer. A 10 nm thick buffer layer of Al₂O₃ was sputtered on a silicon wafer, followed by a 2 nm thick iron catalyst layer. A quartz crystal microbalance was used to monitor the deposition rate and thickness of the catalyst layer during sputtering. A tube furnace with 22 mm inner diameter was used for the CVD processes. Argon (Ar), hydrogen (H₂) and ethylene (C₂H₄) feed gases were regulated with mass flow controllers. After sealing the catalyst substrate in the tube, the ambient atmosphere was removed by vacuum and replaced with the synthesis gases. Flow rates of 56 standard cubic centimeters per minute (sccm) of Ar, 10 sccm of H₂ and 14 sccm of C₂H₄ were maintained through the temperature ramp and CNT synthesis periods. The furnace was ramped to 750 °C in 10 min and then held at that temperature for 25 min. The furnace was cooled to room temperature under a flow of argon. The arrays grew to ~1.4 mm in 25 min.

The as-grown arrays behaved like rigid foam in compression; the deformation of the structure was permanent upon load release. A post-growth CVD treatment step was added to alter the CNT structure within the array. This step provided the desired compressive strength increases, recovery from deformation and ability to tune the foam properties. After completing CNT array growth in 25 min, the growth gases were replaced with pure C₂H₄ for 30 s. Array growth has shown to naturally slow and stop with the buildup of amorphous carbon on catalyst particles exposed to hydrocarbon gases [19]. Here, the high hydrocarbon concentration accelerated amorphous carbon buildup and termination of CNT synthesis occurred within 30 s. The gas flow mixture was reverted back to the original growth formula (56 sccm Ar, 10 sccm H₂ and 14 sccm C₂H₄) after the termination step. The CNT arrays remained in the furnace at a temperature of 750 °C, but no further vertical growth of the CNTs was observed. A series of identical arrays, grown in 25 min, were processed with increasing post-growth treatment times of 0, 35, 65, 95, 125, 155 and 215 min.

Compressive properties of the CNT arrays were measured using a Shimadzu mechanical testing machine. The CNT array samples were mounted on the lower platen and compressive force was applied to the array using a 3.18 mm diameter aluminum compression rod mounted to the load cell, seen in Fig. 1. All of the compression tests were conducted on the interior section of the CNT arrays. This type of loading is different than loading free standing columns of CNTs [20], due to the confinement of the compressed section by the surrounding CNTs within the array. The compressive stresses were calculated using the cross sectional area of the compression rod. Compressive strains were calculated using the displacement of the compression rod. Loading and unloading rates were 2.0 mm per minute. Supporting videos show compression of the outside edge of the array with the sole purpose of making the compression and recovery more visible to the viewer. Both loading and unloading data were collected for 100 cycles at both 60% and 90% strain.

Scanning electron microscopy (SEM) was used to investigate the morphology of the CNT structures. A JEOL 6400F operating at 5 kV was used to capture the images. Samples were mounted to the sample stage with double-sided conductive carbon tape. Transmission electron microscopy (TEM) images were collected in a JEOL 2010F, operating at 200 kV, to measure CNT diameter and wall number. The CNTs were individualized by sonicating in ethanol for 10 min. After dispersing the CNTs, a drop of the solution was placed on a holey carbon TEM grid and allowed to dry. A Renishaw Raman microscope was used to collect the Raman spectrum from as-grown and post-treated CNT array samples. Data was collected from the top surface of the arrays using a 514 nm laser with an approximate spot size of 10 μm.

3. Results and discussion

3.1. Effects of CVD treatment time on CNT array mechanical properties

As-grown CNT arrays were permanently deformed after compressive loading. A morphological change during the post-growth CVD treatment caused the CNT arrays to become resilient and exhibit shape recovery after compression. This change is depicted in Fig. 2 and seen in the compression video in the supporting information. Fig. 3a shows a SEM image of the side of the as-grown CNT array. The SEM image in Fig. 3b shows the same array after the 125 min post-growth treatment, exhibiting only slightly discernible structural changes. TEM images provided a better view of the structural changes that occurred during the post-growth CVD treatment. Fig. 4a
and b shows TEM images of the as-grown CNTs. They had 3–4 walls with a diameter range of 7–9 nm. After the 125 min CVD treatment, the CNTs experienced radial growth (see Fig. 4c and d). CNTs with diameter up to 14 nm were measured. Deposited layers were identified in the highest magnification images with CNTs containing up to 14 walls. Our observation of increase in tube wall number contrast results obtained by Xuesong et al. who used a much faster chemical vapor infiltration process to almost completely fill CNT arrays with pyrolyzed carbon [21].

Density measurements, shown in Fig. 5, indicated an almost linear increase in array density as a function of treatment time. Array density was calculated based on the macroscopic dimensions of the array and the mass of the nanotubes on the substrate, measured by a sensitive microgram balance. The substrate mass was measured prior to CNT growth and subtracted from the total mass after growth. Density increased six fold from 0.018 to 0.114 g cm$^{-3}$. The increase in density was due solely to the increase in thickness of the originally grown CNTs. The height and areal density of the CNTs in the array remained constant before and after the treatment.

Fig. 6a shows the compressive loading–unloading curves for the shortest three treatment times. The as-grown CNT array exhibited a compressive strength similar to that of polymer based open cell foams [22]. However, the CNT array recovered only 4% during the unloading. When the treatment time was increased to 35 min, a partial recovery upon unloading emerged, while at 65 min a complete loading and unloading loop was obtained. Fig. 6b shows the loading–unloading
curves for the remainder of the treatment times. All of the treatment times longer than 65 min exhibited nearly complete recovery upon unloading with the compressive strength rapidly increasing after 125 min. The post-growth CVD treatment time of 215 min produced the highest compressive strength of 6.8 MPa (985 psi).

The arrays compressed to 90% strain produced very similar results, as seen in Fig. 7a. No data was collected for the array treated for 215 min at 90% strain due to cracking and separation of the array from the substrate after the first unloading cycle.

During subsequent compression cycles, the plateau strength of the CNT foam was reduced, while permanent compressive deformation slowly accumulated as the cycle number increased. This trend is shown in Fig. 7b as multiple loading curves, with increasing cycle number displayed. The same trend was recorded for all of the CVD treated samples and also for other CNT array foams that exhibit recovery from compressive deformation [1,2]. A summary of the multi-cycle compressive loading is given in Table 1.

The mechanical properties of the CNT array foams could be tuned for specific applications through changing the treatment time. The longest treatment times produced the highest strengths at the expense of higher density and large permanent deformation after multi-cycle loading. The shortest treatments produced foams suitable for applications requiring multi-cycle loading with very low density requirements. Increasing the treatment time not only increased the com-

Fig. 4 – TEM images of (a) and (b) CNTs from the as-grown CNT array showing 3–4 walls and (c) and (d) CNTs from the array after a 125 min post-growth CVD treatment with up to 14 walls.

Fig. 5 – CNT array foam density plotted as a function of the post-growth CVD treatment time.
pressive strength, it also increased the specific compressive strength. The specific strength doubled after the treatment time was increased from 95 to 155 min and doubled again from 155 to 215 min. The longer treatment times would best suit applications requiring the highest compressive strengths possible, where density and multi-cycle loading are less important design considerations.

The specific strength of the CNT foams is higher than other foam materials with similar densities. The longest treated CNT foam has a specific strength approximately 60× greater than flexible polymeric foams capable of shape recovery [22]. It was also 3–5× greater than rigid polymer foams and aluminum based metal foams with densities less than 0.2 g cm\(^{-3}\) [22–27]. All of the data points for comparison were taken at 60% compressive strain from the literature. In addition, the CNT array foams recovered their shape after load removal, making the material reusable, while aluminum and rigid polymer foams are intended for a single loading event. Analysis of the video of the unloading of the CNT array foam showed that the array recovered from 90% compressive strain in ~0.2 s, an almost immediate recovery.

In addition to excellent compressive strength, the CNT array foams exhibited high thermal resistance. A foam-like CNT array was heated to 500 °C in air for 30 min. Fig. 8 shows the compressive strength of the array prior to and after the thermal treatment. Both of the tests were conducted on the same CNT array in different locations. The loading and unloading curves showed minimal change before and after the treatment. The thermal resistance matches the performance of aluminum foams and far exceeds the operating temperature for polymeric foams. High temperature silicone and polyimide foams have a maximum use temperature of ~250 °C.

Polyurethane foams have a glass transition point of ~50 to ~20 °C [28]. Below this transition point, recovery of the foam will not occur and the total energy absorbed by individual polymer chains decreases. CNTs do not exhibit the major temperature transitions that influence bulk polymer properties. Thus, CNT array foams may be suitable for low temperature energy absorbing applications, such as in space vehicles. Low and high temperature viscoelasticity in foam like CNT structures was recently confirmed by Xu et al. using dynamic mechanical analysis [29] and suggested for applications in extreme environments by Gogotsi [30].

3.2. Strengthening mechanisms

The SEM and TEM images in Figs. 2 and 3 appeared to show that carbon deposited on the CNTs within the array was, for the most part, in the form of additional graphitic layers. Raman spectra were collected for multiple treatment times to confirm this observation. The data was obtained from the CNT arrays before the compression testing. Fig. 9 shows the change in graphite and disordered carbon peaks after CVD treatments of different lengths.

The graphite to disordered peak intensity ratio (\(G/I\)) decreased from 1.28 to 0.95 indicating that the CNTs retained a similar structure after the post-growth CVD treatment. Had the main contributor to the diameter increase been amorphous and disordered carbon, this ratio would have changed more appreciably [31].

The large increases in compressive stress of the CNT foam with increasing treatment time were due to the deposition of carbon material on the as-grown CNTs. The areal density of CNTs within the array remained constant after the treatment, as no new CNTs were grown. Thus, the strengthening of the array can be attributed to two factors: an increase in the diameter of the individual tubes and increases in bonding between tubes.

The critical buckling load of individual tubes of a constant segment length exposed to compressive force is dependent on the elastic modulus of the material, tube diameter and wall thickness. The TEM images in Fig. 4 show large increases in the diameter and tube wall thickness of individual CNTs within the post-growth treated array. A portion of the compressive strength increases seen in this study can be attributed to the radial thickening of the tube wall.
The ultra-high aspect ratio of the CNTs within arrays guarantees that bundling must occur to support mutual vertical growth. It is likely that carbon encapsulated these bundles during the post-growth CVD treatment, increasing the tube–tube bonding at these bundles. Increasing the tube–tube bonding has the effect of decreasing the segment lengths of the CNTs between bonds. The reduction in segment length also increases the critical buckling load. Due to the fact that the buckling wavelength of the CNTs could not be measured in this experiment, it was not possible to determine the relative influence of each of the factors on the compressive property increases.

### 3.3 Compressive recovery of CNT arrays

Although CNTs have extremely high stiffness, they can recover without fracturing after buckling with a very small radius of curvature [32]. This property allows CNT arrays to recover after large compressive deformations and severe buckling of individual tubes. However, recovery after compression of millimeter long CNT arrays has only been documented in a few other reports [1,2]. There, Cao et al. reported that CNTs in their array occupied 13% of the volume. In contrast, the CNT volume fraction for the 125 min treated arrays was 3%, based on the density of the array (0.06 g cm$^{-3}$) and the density of the individual tubes (1.85 g cm$^{-3}$). As this volume fraction was much lower than the previous reports [1,2], it was concluded that having an extremely high volume fraction of CNTs in the array was not critical for recovery.

The bending stiffness of individual CNTs within the array may determine whether or not recovery will occur after unloading. Increasing the tube wall thickness increases the bending stiffness as a function of the change in moment of inertia. However, two results contradict the bending stiffness explanation. First, compression of as-grown arrays, at strains less than 10%, resulted in permanent deformation. At low strain levels permanent local buckling of tube walls is unlikely. Second, another millimeter tall CNT array sample, grown

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**Table 1 – CNT array compressive properties for different CVD treatment times at both 60% and 90% compressive strain ($\varepsilon$)**

<table>
<thead>
<tr>
<th>Treatment time (min)</th>
<th>Density (g cm$^{-3}$)</th>
<th>$\varepsilon = 60%$</th>
<th>$\varepsilon = 90%$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Stress (Mpa) – first cycle</td>
<td>Stress (Mpa) – 100 cycles</td>
</tr>
<tr>
<td>95</td>
<td>0.049</td>
<td>0.7</td>
<td>0.4</td>
</tr>
<tr>
<td>125</td>
<td>0.063</td>
<td>0.9</td>
<td>0.6</td>
</tr>
<tr>
<td>155</td>
<td>0.079</td>
<td>2.3</td>
<td>1.5</td>
</tr>
<tr>
<td>215</td>
<td>0.114</td>
<td>6.8</td>
<td>1.5</td>
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<tr>
<td></td>
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<td>95</td>
<td>0.049</td>
<td>1.6</td>
<td>1.5</td>
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<tr>
<td>125</td>
<td>0.063</td>
<td>2.6</td>
<td>2.3</td>
</tr>
<tr>
<td>155</td>
<td>0.179</td>
<td>4.3</td>
<td>2.9</td>
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<tr>
<td>215</td>
<td>0.114</td>
<td>–</td>
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</tbody>
</table>

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**Fig. 7 – Compressive stress vs. compressive strain loading-unloading curves for (a) samples that were cycled with 90% compressive strain, (b) change in compressive stress for the 155 min treated sample as a function of cycle number (loading only).**
using low pressure CVD of acetylene on iron chloride catalyst, with CNT diameters of approximately 30 nm, showed no recovery after compression. Individual CNTs in the alternate sample had a much larger bending stiffness, due to their much larger diameter, yet shape recovery after compression for those untreated samples did not occur. The recovery of millimeter long CNT arrays has only been reported in two other cases in the literature. With only a very small fraction of CNT array growth studies reporting this recovery after compression feature, we hypothesize that the recovery is a function of the change of the surface of the CNTs after the post-growth CVD treatment.

The most apparent change to the CNT structure was that the CVD deposited layers were much rougher than the smooth walls of the as-grown CNTs. CNTs have an extremely high surface area and their van der Waals interactions are quite significant. This is evident in the difficulty of breaking up bundles of CNTs and their propensity to agglomerate in solution. In an uncompressed CNT array, the tubes are individualized aside from the points where they contact to support the vertical growth. When a CNT array is compressed, segments of the CNTs not previously touching make contact with each other. If the van der Waals interactions among compressed CNTs are significant, the array will remain permanently deformed. This may be the case for the as-grown CNT arrays during compression. Through increasing the surface roughness, the van der Waals interactions among tubes decreases, possibly allowing for the compressed CNTs to separate and unfold as the compressive load is removed. During preparation of TEM samples, a stable dispersion of CNTs in ethanol was much easier to achieve for CNTs that had the post-growth CVD treatment, confirming a reduction in interactions among CNTs. We propose that this mechanism is important in explaining the transition from permanent deformation to recovery during compressive loading and unloading.

4. Conclusions

The compressive properties of CNT arrays were turned using a CVD treatment. The treatment produced radial growth of additional tube walls on CNTs, which led to higher compressive strengths and recovery of the arrays after compression. The strength was tuned by varying the post-growth CVD treatment time; longer treatment times produced the strongest samples. The high compressive strength of the foam-like arrays was derived from the strength of the individual tubes and the mutual support that they provided in the aligned array. The specific compressive strength recorded was superior to polymer and low density aluminum foams, highlighting their potential use in low density energy absorbing applications. Mechanical properties of the CNT array foams were unchanged after exposing samples to a temperature of 500 °C in air for 30 min, making these low density structures acceptable for applications where polymer based foams would be unsuitable.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbon.2011.03.012.

REFERENCES


