Carbon Nanofiber Hybrid Actuators, Part I: Liquid Electrolyte-Based

YUN YEO-HEUNG, ATUL MISKIN, PHIL KANG, SACHIN JAIN, SUHASINI NARASIMHADEVARA, DOUGLAS HURD, VISHAL SHINDE, MARK J. SCHULZ1; VESSELIN SHANOV, PENG HE, F. JAMES BOERIO, DONGLU SHI, SUBRAHMIN SRIVINAS2

1-Mechanical Engineering, Smart Structures Bio-Nanotechnology Laboratory, 2-Chemical and Materials Engineering, University of Cincinnati, Cincinnati, OH 45221

ABSTRACT: This two part paper describes for the first time a Carbon Nanofiber (CNF) – Poly Methylmethacrylate (PMMA) composite material that has electrochemical actuation properties. Part I of the paper considers use of a liquid electrolyte while Part II considers a solid electrolyte. Concerning the Part I, a combination of solvent casting and melt mixing were used to disperse CNF in PMMA, and thin films of the material were cast. A liquid-based electrochemical actuator was formed by placing the CNF Composite film in an electrolyte solution. Electrochemical Impedance Spectroscopy was carried out to characterize the electrochemical properties of the PMMA-CNFR actuator. The actuator was tested at voltages up to 15 volts and the relationship between displacement and applied voltage was determined. Compared to previous single wall carbon nanotube buckypaper actuators, the CNF-PMMA composite actuator is stronger and is two orders of magnitude lower in cost, but needs higher voltage to actuate. Because of the low cost of the CNF Hybrid Material and the possibility for using stronger host materials, a new class of Smart Structural Materials that enable whole structures to actuate may become feasible.

Key words: Carbon Nanofiber, Hybrid Actuator, Liquid Electrolyte, Smart Structural Material.

INTRODUCTION

The discovery of Multi-Wall Carbon Nanotubes (MWCNT) by (Iijima 1991), and the C60 fullerene and Single Wall Carbon Nanotubes (SWCNTs) (Benning et al, 1992) opened the possibility for a new class of smart materials based on nanoscale materials. In 1999, electrochemical actuation of SWCNT was developed by (Baughman et al, 1999); in 2001 the piezoelectric effect in Carbon Nanotubes (CNT), and Boron Nitride Nanotubes (BNT), was studied (Nakhmanson et al., 2003; Lebedev et al, 2001; Nakhmanson et al, 2002), and experiments to study the actuation properties of a single CNT were begun, and an electrostatic array actuator was investigated (Gao et al., 2000). In 2002 improvements in CNT actuation were developed, and in 2003 Vanadium Oxide Nanotubes (VNT) were used for actuation (Gu et al, 2003). Of these new smart materials, the electrochemically induced strain of CNT is particularly important. In theory, the CNT can provide higher actuation performance (up to 10x strain and 29x energy density) than piezoelectrics, although the bandwidth of the CNT actuation is small. Comparing the various types of new smart materials including ionic polymers, vanadium oxide nanotubes, zinc oxide nanowires, silicon nitride and silicon carbide nanotubes, boron nitride nanotubes, titania nanotubes, and all the existing smart materials such as piezoelectrics and shape memory alloys, it appears that CNTs have an advantageous combination of large strain, large strength, large actuation force, light weight, and acceptable bandwidth for use in several applications. However, achieving these properties at the macroscale has been very difficult. Transferring charge to the tubes in a SWCNT actuator and transferring the shear load through the actuator have been limitations to realizing the theoretically predicted 2% strain and high performance of SWCNT actuators/sensors. Recently Ray Baughman and his group at the University of Texas at Dallas (Fraysse et al, 2002; Barisci et al, 2003) have made great progress in spinning CNT fibers. The spun fibers are microns in diameter and the strength is greatly improved compared to previous CNT fibers. A compromise involved in making strong fibers is that the nanoscale actuation properties may be reduced because it is difficult to intercalate ions into the interior of the dense fibers, and these fibers are made using SWCNTs which are too expensive for many applications. To avoid the reduction in actuation of dense fibers, the low strength...
of buckypaper actuators, and the high cost of SWCNT actuators, we may be the first to have built and tested a multi-wall Carbon Nanofiber (CNF)-PMMA electrochemical actuator. This hybrid actuator material has somewhat lower strain than SWCNT-based materials, but it is about 200 times lower in cost than SWCNT actuators.

This paper describes the initial development of electrochemically actuated hybrid materials using CNF. The development started by trying to make buckypaper using the CNF. It is very difficult to make CNF buckypaper because the van der Waals forces are small compared to the SWCNT. However, by using 3M tape we showed the electrochemical actuation properties of CNFs. Then we considered two methods of fabricating CNF-PMMA actuators. The first, a layer by layer method is used to build-up a CNF-PMMA actuator. The second method is to synthesize the CNF-PMMA hybrid actuator material using the solution casing method. These two actuator types were tested in an electrolyte solution. Also, Electrochemical Impedance Spectroscopy (EIS) was carried out to characterize the electrochemical properties of the material. Since EIS can provide the frequency-dependent complex impedance of an electrochemical cell, this result is directly related to the dopant concentration of the liquid-based actuator. The actuation properties of these two types of actuator were studied in a preliminary way based on the relationship between applied voltage and deflection of cantilevered beams. The first results on testing CNF Hybrid actuators are presented in this paper. Since this is a new material, the properties optimization and detailed characterization of the material are just beginning.

NANOTUBE MATERIALS

There are becoming many different types of nanotubes and nanostructured materials, and the terminology used to describe them is not universal. Therefore, a list of some of the different types of nanotubes and nanofibers is given in Table 1 as background information for researchers who are new to the field of nanoscale smart materials. The acronym for a Carbon Nanotube is CNT. The number of walls is described as; Single Wall (SW), Double Wall (DW), and Multi-Wall (MW). The nanotube may be amorphous or crystalline. Bamboo nanotubes have internal closeouts along the length of the tube and this occurs in Boron Nitride (BNT) nanotubes and in some MWCNT due to the base growth mechanism. SWCNT have one wall and diameters of about 1.4 nm; MWCNT have multiple walls and diameters of 10 nm and larger; CNF have multiple concentric walls and have diameters of 65 nm or larger. For comparison, graphite fibers used in traditional composite materials have diameters on the order of six thousand nm. Carbon Nanofibers (CNF) are similar to MWCNT but there is an important difference - in the nanofiber the graphene cylinders are not parallel to the fiber axis. They are at an angle of 20 degrees to the fiber axis in a Dixie cup arrangement and terminate at the walls of the next outer tube.

<table>
<thead>
<tr>
<th>Type and Description</th>
<th>Designation of Nanotubes</th>
</tr>
</thead>
</table>
| SWCNT- 0.3-2 nm D, 200-1000 nm L; grown by catalyzed CVD and other methods, cost purified is ~$500/gram (Carbon Nanotechnologies Inc.) | SiC Nanotubes; 2-4 nm D, 1-50 micron L; grown by CVD of SiOx Nanostuctures (NASA Glenn Research Center)
| DWCNT- 2-4 nm D, 1-50 micron L, grown by CVD of methane over cobalt nanoparticles supported on porous MgO nanoparticles (Nanolab) | Vanadium Oxide- V2O5 Nanotubes (VNT), 15-100 nm D, MW
| MWCNT- 10-50nm Dia., 1-50 micron length, grown by CVD; also bamboo MWCNT 20-40 nm Dia., 1-20 micron length, internal closeouts, ~$150 gram (FirstNano, Inc.) | Boron Nitride Nanotubes- (BNT) 3-40 nm D, 40-80 nm D bamboo/cone nanotubes and nanosize polyhedral particles in clusters (Australian National University)
| Carbon Nanofiber, Pyrograf III trade name- (CNF) 70-200 nm D, 50-100 micron L; non-concentric nested tubes walls angled 20 degrees to the longitudinal axis, carbon crystal structure, vapor produced decomposing hydrocarbons and catalyst, hydrogen sulfide, ammonia, different grades: ~$100/lb (Applied Sciences Inc) | Silicon Carbide Nanotubes- (SiCNT), 200 nm D, 60 micron length, amorphous nanocrystalline (NASA Glenn Research Center)
| | SiOx Nanostructures- 20-30 nm D tubes, bundles, amorphous, thermal evaporation |

Besides nanotubes and nanofibers, there are other nanostructured materials including nanobelts, nanoribbons, nanowires, nanoplates, nanonails, etc. which are not common, and are mostly under development and are not discussed here. Some of the important differences in the nanotubes/nanostructures are discussed next. The type of nanotube affects the processing method for smart materials; SWCNT are the smallest diameter and the most difficult to process and the most expensive. The MWCNT do not have as high or varied properties, but are easier to process because of their larger diameter. While CNF are similar to large diameter MWCNT, the nanofibers are not continuous tubes and their surfaces show steps at the termination of each tube wall. The nanofibers include PR-24 (~65nm dia) and the PR-19 (~130nm dia). The PR-19 have a CVD layer with a turbostratic carbon layer parallel to the surface and these fibers may be more robust to breakage, but the
electrical properties of the nanofiber are changed by the coating. The PR-24 do not have a CVD coating. There are low and high density variations of these two nanofiber types. The low density nanofibers are longer and more difficult to disperse in host materials and polymers, while the high density nanofibers are shorter and disperse easier and may have the best mechanical properties. The low heat treatment of nanofibers improves thermal, electrical and mechanical properties and the dispersion properties and is designated by LHT. The high heat treatment removes iron to less than 1.4% and is designated by HHT. The iron may still be inside the fiber. Heat treating at 2,900 deg C in an inert atmosphere is used for purification. An oxygen atmosphere would cause the nanofibers to burn at high temperature. No solution purification is used for nanofiber processing. The nanofibers would sublime above 3,000 deg C. The PS designation of nanofibers indicates the fibers have been pyrolitically stripped. Nanofibers can be functionalized using oxygen or nitrogen groups to improve adhesion to polymers.

There are three types of carbon nanotube raw materials that have potential for use as electrochemical actuators and smart materials: (i) SWCNT which have excellent electrochemical properties, but the cost is very high, and incorporating the nanotubes into polymers at high loadings is difficult; (ii) MWCNT which have good electrochemical properties, the cost is moderate, and incorporating the nanotubes into polymers may be possible by growing arrays of nanotubes and casting the polymer around the arrays; and (iii) CNF in which the electrochemical properties are good, the cost is low, and incorporating the nanofibers into polymers is somewhat easier because the fibers are large. All three materials alone or in combination can be used to develop intelligent materials. The SWCNT can be purchased commercially or can be grown using a nanofurnace (FirstNano Inc.); the MWCNT can be purchased commercially and grown in arrays; and the CNF can be purchased commercially. A nanotube synthesis laboratory using Chemical Vapor Deposition (CVD) is a feasible way for engineers to make nanotube materials. A commercial nanofurnace (Smart Structures Bio-Nanotechnology Laboratory) with recipe-driven software allows precise and accurate control of nanotube growth with fully programmable feedback loops, short gas paths, and automatic logging of gas flow and thermocouple data for error-free analysis with user-favorite software.

**ACTUATOR FABRICATION**

The CNF is first dispersed alone in a solvent defines as solvent 1 by shear mixing for 5 hours and then ultrasonication for 2 hours, see Figure 1. PMMA and then a solvent 2 are used in the present study. The PMMA was dried before use in a vacuum oven at 50, 60, and 70 °C, respectively, under 10^{-3} Torr pressure for 5 h. Using solvent 2, PMMA first is melted and this solution was stirred and heated continuously at 70 °C for several hours until the mixture became a homogeneous solution. The CNF-solvent 1 solution was then slowly added to polymer solution under constant stirring. Excess solvent was removed by slow evaporation.

![Figure 1. Simultaneous ultrasonication and shear mixing.](image1)

![Figure 2. Two different methods to fabricate the CNF-PMMA actuator; (a) CNF-PMMA solution casting, and (b) individual-layers to form the CNF-PMMA.](image2)
This final solution is cast in a designed mold and evaporated at room temperature under vacuum. In this paper, we considered two different methods to make CNF based electrochemical actuators. First, shown in Figure 2(a), we synthesized the CNF-PMMA composite actuator with different weight % of CNF. The CNF-PMMA composite is bonded on 3M tape as an electrochemical inert layer. The second method is shown in Figure 2(b) where two separate layers are used to produce the CNF actuation property. The individual layers type actuator is tested for comparison with the CNF-PMMA composite actuator.

This actuator film was cut into strips with the geometry $0.7 \times 2 \times 0.02$ cm and the films had low resistance between 400 $\Omega$ and 700 $\Omega$ and weighed 0.07 g. The CNF were randomly aligned and not well dispersed, and the Young’s modulus was about the same as the PMMA material, about 1 GPa. However, there are several techniques that will be investigated to make strong materials. After cutting to size, Mylar tape is used to make an electrochemical inert layer. Figure 3 shows the processing of the CNF-Composite Material.

**ELECTROCHEMICAL IMPEDANCE**

The EIS was performed on three-electrode cells, with the CNF-PMMA actuator as the working electrode, a Platinum Wire used as the Reference Electrode, and a Platinum plate as the counter electrode. EIS measurements were performed using a Gamry Potentiostat (Model: PCI4/750) coupled with the EIS (Gamry, EIS300) software (Figure 4). The cell was equilibrated for several hours after each step. An electrolyte solution is used for the experiments.

![Figure 4. EIS setup for the wet actuator using Gamry instrumentation.](image_url)

![Figure 5. EIS at cell potentials of 0.1 to 0.4 V; (a) 0.05Hz to 100KHz, and (b) enlarged view of high frequencies between 100Hz-100KHz.](image_url)

The impedance spectra were measured using 10mV rms amplitude at frequencies between 0.05Hz and 100KHz. Figure 5 shows the EIS data (Nyquist plot) with imaginary (Capacitive) vs real (Resistive) components of the complex impedance; we tested four
different potentials; 0.1 V, 0.2 V, 0.3 V, and 0.4 V. Figure 5(a) represents the spectra for frequencies between 0.05Hz and 100KHz. Small depressed semicircles were observed at higher frequencies in Figure 5(b), and second larger capacitive loops appeared at lower frequencies in Figure 5(a). The radius of these second larger capacitive loops at lower frequencies can explain the mass transport of the charge balancing ions (Clay et al, 2000). Lines drawn through the rising part of the second loops at 45° angles represent the Warburg impedance which appears at intermediate frequencies. This Warburg impedance indicates the finite diffusion of ions in the wet actuator. Also, we can see the Warburg impedance at very low frequency with an intermediate open circuit potential 0.1 V, and 0.2 V. With the high open circuit potential at very low frequencies, the curving of the plots moves back to the real axis which indicates that the impedance may be limited by convective steady state diffusion (Park and Yoo, 2003). Again, as shown in Figure 5, the response is largely capacitive and $Z_{\text{mag}}$ decreases with decreasing potential at a fixed frequency which represents the working electrode attracting ions, and this characteristic matches the ionic behavior reported in references (Park and Yoo, 2003).

In the case of the wet actuator, the capacitance has to be large enough to charge the ions and actuate the CNF. However, in order to get larger displacements, we have to apply higher voltage, and, necessarily, this lowers the capacitance of the wet actuator. This might be the reason why high voltage degrades the life cycle of the wet actuator. This Warburg impedance term is removed. Therefore, the impedance spectra can be modeled as Randles’s Circuit. As shown in Figure 6(b), the simple equivalent circuit model matched the experimental results pretty well. As shown in Table 2, the double layer capacitance is on the order of 15-30 $\mu$F with a 2 cm$^2$ actuator area. Thus, the double layer capacitance of the PMMA-CNF composite actuator in electrolyte solution is about 8-15 $\mu$F/cm$^2$, which is consistent with the macroscopic surface area of buckypaper strips (Park and Yoo, 2003).

$$Z(\omega) = R_x + R_p \left[ 1 + \frac{\lambda}{2\omega} \right] - R_p \omega^2 C_d - \frac{jR_p \lambda}{\sqrt{2\omega}}$$

in which $C_d$ is the double layer capacitor; $R_p$ is the polarization resistance; $R_s$ is the solution resistance, $\lambda = \kappa_f / \sqrt{D_0 + \kappa_b / \sqrt{D_R}}$, $\kappa_f$ and $\kappa_b$ are the forward and backward electron-transfer rate constants, respectively, $D_0$ and $D_R$ are the diffusion coefficients, and $\lambda / \sqrt{2\omega}$ is called Warburg impedance (Park and Yoo, 2003). In the case of open circuit voltage, 0.3 V, and 0.4 V, the Warburg impedance term is removed. Therefore, the impedance spectra can be modeled as Randles’s Circuit. As shown in Figure 6(b), the simple equivalent circuit model matched the experimental results pretty well. As shown in Table 2, the double layer capacitance of the PMMA-CNF composite actuator in electrolyte solution is about 8-15 $\mu$F/cm$^2$, which is consistent with the macroscopic surface area of buckypaper strips (Park and Yoo, 2003).

Table 2. Estimated parameters for the equivalent circuit model with four differential potentials.

<table>
<thead>
<tr>
<th>Open circuit potential</th>
<th>$R_p$</th>
<th>$R_s$</th>
<th>$R_{\text{Warburg}}$</th>
<th>$C_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 V</td>
<td>2 K $\Omega$</td>
<td>141 $\Omega$</td>
<td>328e-6 S</td>
<td>17.67</td>
</tr>
<tr>
<td>0.2 V</td>
<td>2.1 K $\Omega$</td>
<td>141 $\Omega$</td>
<td>326e-6 S</td>
<td>17.67</td>
</tr>
<tr>
<td>0.3 V</td>
<td>3.9 K $\Omega$</td>
<td>154 $\Omega$</td>
<td>-</td>
<td>32.50</td>
</tr>
<tr>
<td>0.4 V</td>
<td>2.5 K $\Omega$</td>
<td>156 $\Omega$</td>
<td>-</td>
<td>13.50</td>
</tr>
</tbody>
</table>

**EXPERIMENTATION**

Figure 7(a) shows the operational amplifier circuit. In order to supply enough power from the NI board, a voltage follower is used and a noninverting amplifier is designed using a commercial operational amplifier. Figure 7(b) shows the experimental setup for the CNF-PMMA composite actuator. These aqueous-based actuators are immersed in the electrolyte solution. Square wave potentials are applied between the platinum counter electrode and working electrode. Displacement of the CNF-PMMA actuator is measured using a laser displacement sensor (Keyence, LC-2400 Series). The square wave amplitude is up to 15 V and applied frequencies range from 0.2 to 10 Hz. The signal is controlled by PCI 6036 NI board. Figure 8 shows the experimental setup built for characterizing electrochemical nanotubes actuators. The controller is designed based on a LabView VI.
CNF-PMMA ACTUATOR RESULTS

A Scanning Electron Microscope (SEM) image of the cross section of the PMMA-CNF composite actuator is shown in Figure 9. The dispersion and adhesion of the fibers need to be improved to increase the performance of the actuator.

Figure 10 shows the relationship between the deflection of the cantilever beam tip and the voltage applied to the CNF-PMMA individual layer actuator. The applied potential was found to influence the strain rate in electrochemically driven CNF wet actuators. Typically, with all the results, increasing the magnitude of the applied potential increases the strain rate. It is likely that higher potentials increase the charge accumulation at the CNF/electrolyte interface and cause the faster response and higher strain (Schulz et al, 2005). However, the higher voltages would degrade the CNF actuator and decrease the lifetime. Therefore, there is a limitation to increasing voltage to achieve a high strain rate. With the increase of frequency, the deflection of the CNF actuator decreases. This CNF-PMMA individual layer actuator can be used as multi-layers actuators for large strain and to be manufactured into various geometries such as rectangular and circular plates, tubes, rods, and also complex shapes.

Figure 11 shows the deflection results for the CNF-PMMA composite actuator. As you can see, the composite actuator has similar actuation properties as the layered actuator. With an increase of the frequency of the square wave, deflection of the cantilever beam actuator decreases. Also, with the increase of potential, the deflection of the cantilever beam actuator increases. Again, higher potential causes greater charge accumulation at the CNF/electrolyte interface and causes the faster response and higher strain. However, higher voltage may degrade the actuator and decrease its lifetime. Therefore, there is a limitation to increasing voltage for high strain rate.
Figure 10. Deflection of the individual layer actuator beam due to a square wave input of 8V at frequencies of; (a) 0.2Hz; (b) 0.5Hz; (c) 1Hz, and (d) 5Hz.

Figure 11. Deflection of the composite actuator beam due to a square wave input of 10V at frequencies of; (a) 0.2Hz and (b) 0.5Hz (c) 1Hz and (d) 5Hz.
Figure 11 shows the deflection waveforms with the applied potential for the CNF-PMMA composite actuator. These waveform shapes are being studied to provide understanding of the electrochemical actuation mechanism and the stiffness properties of the material. As you can see, this CNF-PMMA composite actuator has similar actuation properties to the layered actuator. With the increase of the square wave frequency, the deflection of the cantilever beam actuator decreases, and also with the increase of potential, the deflection of the cantilever beam actuator increases, as shown in Figure 12. Again, the higher potential causes the greater charge accumulation at the CNF electrode interface and causes the faster response and higher strain. However, the higher voltage will degrade the CNF actuator and decrease the lifetime. Therefore, there is also a limitation to increasing voltage to achieve a high strain rate.

The actuation of the CNF-PMMA composite strip is shown in Figure 13. Very large actuation at 15 volts can occur. This is due to surface actuation and due to poor dispersion of the CNF, and because the bending occurs mostly near the top of the actuator. This is because of shunting in the electrolyte and because the resistance of the actuator reduces the voltage in the lower part of the actuator. These results indicate that large improvement can be made in the design and material processing of the actuator. Besides actuations, carbon nanotubes/nanofiber hybrid materials have been used to form piezoresistive sensors, an amperometric biosensor, and a power generator, see (Smart Structures Bio-Nanotechnology Laboratory). These early results indicate that nanoscale intelligent materials will be a useful and enabling new smart material. More details of the material tested in this paper are given in (Yeo-Heung et al, 2004).

CONCLUSIONS

In the SWCNT, the van der Waals forces do not provide efficient shear transfer for smart structures applications. Therefore, this paper focused on developing a host polymer for nanotubes/nanofibers to provide simultaneous actuation and structural strength. Carbon nanofibers were used because of their low cost. Based on the experimental results and EIS testing, we verified that the electrochemical CNF-PMMA hybrid actuator is a new smart structural material. It is anticipated that continued research will lead to; (i) better dispersion of the CNF, (ii) stronger bonding of the CNF to a stronger polymer, (iii) alignment of the CNF, and (iv) improved efficiency through encapsulation and surface electroding. This will significantly improve the performance of the actuator and produce a multi-functional material that is load-bearing and also has an actuation capability. Rather than bonding piezoelectric materials onto structures to produce actuation, we envision CNF-Hybrid structural materials that can be used to build large structures that self-actuate.

REFERENCES

Applied Sciences Inc., and Pyrograf Products, Inc., contact person, Mr. David Burton.


Carbon Nanotechnologies Inc., 16200 Park Row, Houston, TX 77084-5159, www.cnanotech.com, contact person, Mr. Tom Pittstick.


FirstNano, Inc., 5571 Ekwill St., Santa Barbara, California 93111.


Nanolab, Inc., info@nano-lab.com.


Smart Structures Bio-Nanotechnology Laboratory, University of Cincinnati, Cincinnati, Ohio, 45221, http://www.min.uc.edu/~mschulz/smartlab/smartlab.html.