Building Smart Materials using Carbon Nanotubes

Sachin Jain[a], Phil Kang[a], Yun Yeo-Heung[a], Tony He[a], Sri Laxmi Pammi[a], Atul Muskin[a], Suhasini Narsimhadevara[a], Douglas Hurd[a], Mark J. Schulz[a], Jennifer Chase[b], Srinivas Subramaniam[b], Vesselin Shanov[b], F. James Boerio[b], Donglu Shi[b], Rob Gilliland[c], David Mast[d], and Chris Sloan[e]

[a]Smart Structures Bio-Nano Lab, Mechanical Engineering, [b]Chemical & Materials Engineering,
[c]Electrical and Computer Engineering, [d]Physics, University of Cincinnati, Cincinnati, OH 45221
[e]FirstNano, Inc., 1015 Mark Avenue, Carpinteria, CA 93013

ABSTRACT

The paper discusses the development of polymer composite materials based on carbon nanotubes. Carbon Nanotubes can be used to form polymer hybrid materials that have good elastic properties, piezoresistive sensing, and electrochemical actuation. Of particular interest are smart nanocomposite materials that are strong and self-sensing for structural health monitoring, or self-actuating to improve the performance and efficiency of structures and devices. Since nanoscale research is broad, challenging, and interdepartmental, undergraduate through Ph.D. level students and faculty have combined efforts to attack the special problems related to building nanoscale smart materials. This paper gives an overview of the work being performed to manufacture polymer nanocomposite materials starting from nanotube synthesis through to device fabrication and testing. Synthesis is performed using an EasyTube Nanofurnace, functionalization is done using plasma coating, dispersion using rotary mixing and ultrasonication, and processing using vacuum and pressure casting. Reinforced polymers, a carbon nanotube solid polymer electrolyte actuator, and piezoresistive sensors are being developed for several potential applications. The materials produced indicate that carbon nanotube hybrid smart materials may become a new class of smart material with unique properties and applications, but much work still needs to be done to realize their full potential.

Keywords: Carbon nanotubes, smart structures, nanocomposite, piezoresistive, electrochemical.

1. INTRODUCTION

Single Wall Carbon Nanotubes (SWCNT) have extraordinary mechanical and electrical properties which in many cases exceed those of any other material [1-7]. These superior properties include a 1 TPa elastic modulus, 50 GPa strength, electrochemical actuation, and high thermal and electric conductivities. These properties generally surpass the properties of Multi-Walled Carbon Nanotubes (MWCNT), which are a concentric arrangement of single wall nanotubes. Potential applications of Carbon Nanotubes (CNT) include high strength composites, electrochemical and piezoresistive sensors, and electrochemical actuators. The electrochemical actuation property of CNTs may provide higher actuation performance (about 5x strain and 10x energy density) than piezoelectric materials, and also higher performance when compared to other nanotubes made of elements like vanadium, silicon, boron, and titania. The CNTs actuate due to electrochemical charge injection and bond expansion in an electrolyte. Mats of carbon nanotubes can be formed using van der Waals attraction and actuated in an electrolyte, but the strength and actuation performance are far below the predicted performance using this material. Fibers spun from CNT have shown great mechanical properties [8-11], the actuation and sensing properties will depend on how effective the ion exchange is to the nanotubes in the interior of the fiber. Another approach is to cast the carbon nanotubes in a conductive polymer to attempt to gain good ion exchange and good shear load transfer. The conductive polymer provides strength and when hydrated allows actuation and is discussed in this paper. Overall, the CNT mat/fiber/conductive polymer materials are predicted to open up an enabling new type of smart material that will improve the way we generate and measure motion in devices from the nanoscale to the macroscale. Unlike other smart materials, the CNT based material is simultaneously a structural material because it is load bearing, a functional material because of its electro-mechanical properties that can be tailored, and a smart material due to actuation and sensing. In this paper we describe efforts to make carbon nanotube polymer composite materials for reinforcement, sensing, and actuation starting from nanotube synthesis all the way to device fabrication.

2. NANOTUBE SYNTHESIS

Currently there are three principal techniques to produce high quality SWCNTs, laser ablation, electric arc discharge, and Chemical Vapor Deposition (CVD), [2, 12-24]. Both the laser ablation and arc discharge techniques are limited in the volume of sample they can produce in comparison to the size of the carbon source. In addition, more impurities accompany the nanotubes in the form of amorphous carbon and catalyst particles. The CVD method is a continuous process and currently is the best-known technique for high yield-low impurity production of CNT. Also CVD when supplemented with a plasma generating and controlling facility has the capability to control the size, shape and alignment of the nanotubes. CVD is a gas phase technique, which uses carbon source feed gases such as benzene, methane, acetylene and carbon monoxide. The principle by which the process works is by cracking and decomposition of the carbon source gas molecules at high temperature over the catalyst, which is on the substrate. Alumina-aerogel-supported Fe/Mo is one type of substrate/catalyst combination. The selection and preparation of the substrate/catalyst are important aspects related to nanotube yield and the ability to purify the nanotubes.

An EasyTube nanofurnace shown in Figure 1(a) is used at the University of Cincinnati for the synthesis of carbon nanotubes. The furnace uses the thermally driven CVD process and consists of two main units; the control unit, and the process unit [20-22]. The control unit contains the operator's workstation shown in Figure 1(b), which is a computer controller to operate the furnace. The computer uses the Microsoft Windows environment and LABVIEW as the programming language. The process unit is comprised of; (i) a gas cabinet, (ii) furnace, and (iii) a loader. The system uses four process gases; Methane, Ethylene, Hydrogen, and Argon, which are involved in the production of nanotubes. Nitrogen, the fifth gas is used for operating the gas valves in the furnace. Methane and ethylene are the carbon source gases; argon is used for creating an inert atmosphere. The furnace and sample on the loader in the quartz tube are shown in Figure 1(c). Hydrogen is used for moderating the chemical reaction of the hydrocarbon decomposition. Safety is a concern when using a nanofurnace and combustible gases. The EasyTube nanofurnace has several safety features, and for further safety we have enclosed the furnace in a large fume hood with safety glass doors and installed gas leak detectors in the gas cabinet and all along the gas lines to the furnace.

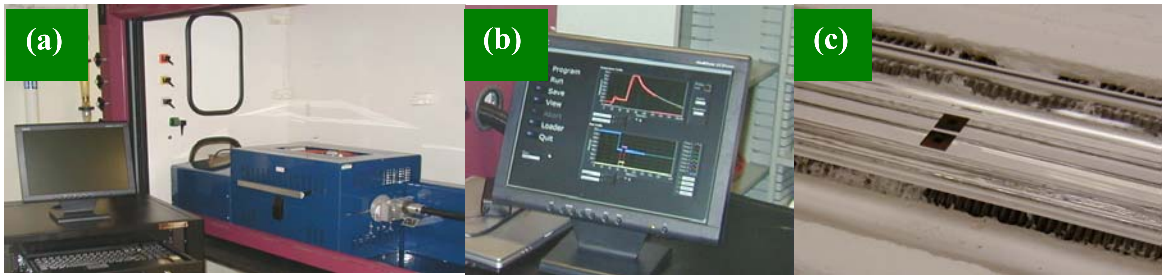

Figure 1. CVD nanofurnace; (a) controller and process unit, (b) display of process temperature and flow rates, (c) two samples on the loader in the quartz tube.

Mass flow controllers control the flow rate of the gases. The gases enter the furnace in the quartz tube where they are heated to a temperature of 900-1000^{o}C. The gas pressures are near atmospheric in the furnace. The hydrocarbons decompose in the quartz tube over a catalyst, which is mounted on a substrate. The catalysts used in the experiments include iron nitrate, alumina, and magneusium oxide. A quartz boat or molybdenum boat are used with a powered support and catalyst for bulk nanotube growth. For high purity nanotubes, the catalyst/substrate deposited on a silicon oxide wafer. The catalyst was deposited at the center of the substrate and spun to control the thickness of the layer of the substrate and catalyst. The substrate was patterned by a lithography technique. Finally the substrate was inserted inside the quartz tube automatically using the loader which is a quartz loader tray driven by the computer. The standard recipe in the furnace to produce high yield/high purity SWCNT runs in three steps, namely: (i) maximum ramp, (2) deposition, and (3) cooling. In the maximum ramp step, the temperature of the furnace is raised from ambient to 900^{o}C in 12 minutes. A continuous flow of argon is used to properly purge the system. Once the temperature reaches 900^{o}C, it is maintained for 10 minutes. This is the deposition stage. Nanotube production occurs in the deposition stage when the supply of argon is stopped and the carbon source gases methane and ethylene are run for 10 minutes with also a flow of hydrogen. The next cycle is the cooling cycle. After the nanotubes are produced they must be cooled to ambient conditions. During cooling the methane, ethylene and hydrogen supply is stopped and the system is again purged with inert argon gas. Apart from these 3 basic steps, a 4th step called the timed ramp can also be incorporated. Unlike maximum ramp, in which temperature rises as fast as possible, in the timed ramp the temperature rises gradually. The process variables responsible for nanotube growth include; cycle temperature, cycle run time, gas mass/volume flow rates, the order and duration of the process steps, and the type and quantity of the catalyst and substrate. These process variables determine the yield and quality of the nanotubes synthesized. Manipulating any one of them can lead to change in size, shape, or density of the nanotubes. Hence, experiments were performed to determine the optimum settings required for the process variables for the nanofurnace. Many experiments were run manipulating the process variables. These included: (1) FirstNano standard recipe for high yield SWCNT [21]; (2) long starting purge with argon at elevated temperature; (3) long deposition growth; (4) higher temperaturte; and (5) several combinations of UC substrate/catalysts and processing steps. Table 1 lists the detailed process conditions for the standard recipe for nanotube growth. The ambient temperature during the synthesis study was about 25°C. The following sections describe two characterization techniques used and the results obtained to determine the type, size, and relative density of the nanotubes grown in some of the synthesis experiments.

Table 1. Standard recipe for high yield SWCNT, experiment 1.

Step	**Type**	**Temperature (°C)**		**Time (min)**	**Flow Rate (SCCM)**			
		Start	**End**		**Hydrogen**	**Methane**	**Ethylene**	**Argon**
1	Heat	Ambient	900	12	0	0	0	1000
2	Deposition	900	900	10	300	1200	30	0
3	Cool	900	Ambient	120	0	0	0	1000

3. SCANNING ELECTRON MICROSCOPY CHARACTERIZATION

A FEI XL-30 ESEM FEG has been used in some of the characterization of the SWCNT. A Shottky hot-field emission tip is employed as the electron source and has an ultimate resolution of 1.2-1.5nm. A large specimen chamber housing a motorized stage with an internal CCD camera allows for insertion and monitoring of fairly large specimens. The ESEM makes use of variable pressure limiting apertures, which allows for chamber pressures between 1-20 Torr. Gaseous detection systems are used in imaging of the samples. Partial ionization of the chamber gas results in charge neutralization at the sample surface, with the oppositely charged particles being collected by the gaseous secondary detector through a cascade effect, resulting in improved signal. High-resolution imaging and characterization of hydrated samples, damage prone samples and insulators can be carried out in the unmodified, uncoated state using ESEM gas based detection methods. The SWCNT are synthesized on a SiO_2/Si substrate or else are in the powder condition. The silicon substrate can be directly mounted on to a standard aluminum mount using double sided carbon adhesive tape. No further sample preparation or metallization is carried out, allowing for the nanotubes to be imaged in their natural condition. A large field gaseous secondary detector without any pressure limiting apertures has been used for imaging of the samples. A maximum chamber pressure of 1.5 Torr can be achieved for using the above setup. A working distance between 8-10 mm, an accelerating voltage of 10-30 KV, and a chamber pressure ranging between 0.9-1.3 Torr have been used and found to be suitable in obtaining high-resolution images of the nanotubes. The ESEM images of the SWCNT produced using the different recipes are discussed in the following sections. Highlights for some of the different processing conditions are discussed.

The tubes produced by the standard recipe [21] corresponding to experiment 1 and the nanotubes based on the process parameters in Table 1 were examined using the ESEM. The tubes were on the order of 1 micron long and 4-10 nanometers in diameter, and meet the estimated dimensional specifications for SWCNT. The nanotubes formed a spaghetti type of pattern with tubes overlying over each other. Figure 2 illustrates unpurified nanotube growth on silicon wafers. Figure 2(a) shows growth of SWCNT using a catalyst on a silicon wafer. Figure 2(b) shows growth of SWCNT between catalyst particles on a silicon wafer indicating that CNT could be grown between catalyst patterns. Figures 2(c, d) show ribbon and sheet-like structures from catalyst on a silicon wafer, and sheet-like structures from catalyst on a glass boat. In all these images the acceleration voltage is 30 kV. Excessive unused shining catalyst is present below the nanotubes, as shown in Figure 2(a). An interesting phenomenon was observed in Figure 2(b). One can see at the right end long SWCNT's originating from one mound of catalyst and terminating at a different mound of catalyst running over the dark silicon dioxide substrate. These long tubes may have been formed in the direction of flow of the gases in the quartz tube. This suggests the possibility for the direct growth of nanotubes between patterned substrates in possibly three dimensions. Another interesting observation not shown is the occurrence of flat ribbon-like structures or ropes of nanotubes. Their large width and long length could be a useful for many applications. Further investigation is being done using High Resolution Transmission Electron Microscopy (HRTEM) and X-Ray Photoelectron Spectroscopy (XPS) to give more details on the type of nanotubes produced and what materials and impurities are shown in the images.

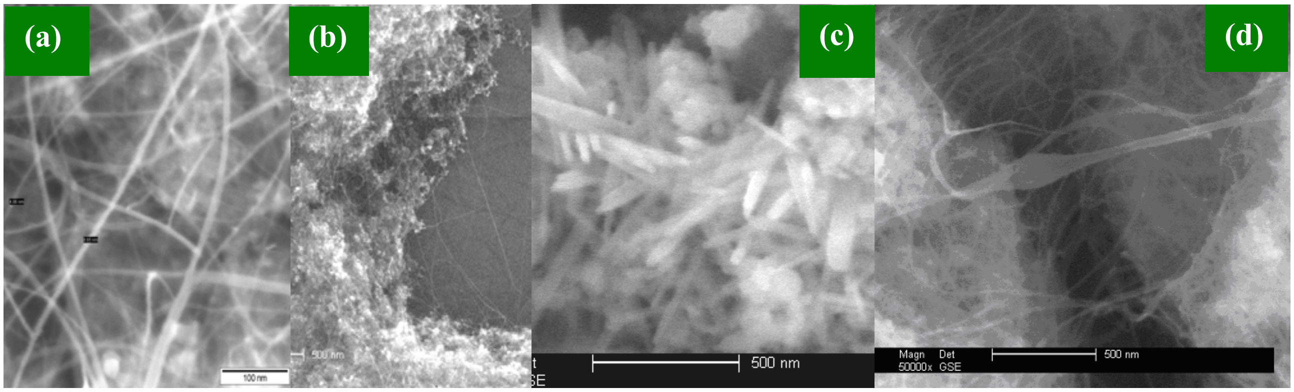

Figure 2. Unpurified nanotubes grown using an alumina substrate; (a) growth of SWCNT above catalyst on a silicon wafer, (b) growth of SWCNT between catalyst on a silicon wafer, (c) obelisk-like structures from a substrate and catalyst on a glass boat, and (d) sheet-like structures from catalyst on a glass boat.

Figure 3 illustrates bulk nanotube growth using a powder substrate and catalyst in a boat. The catalyst and purification methods were developed by UC for high yield easily purified nanotubes. The images shown contain SWCNT and ropes of SWCNT. Figure 3(a) shows the unpurified sample of growth of SWCNT using a powder catalyst and the UC recipe for growth. The difficulties with bulk growth are that the substrate and catalyst are often difficult to remove in the purification process. Figure 3(b) shows purified SWCNT. Figure 3(c) shows purified SWCNT close up. The CaO substrate used was prepared by rotary mixing and ultrasonication and is easy to purify using HCl. An iron based catalyst is used with the CaO substrate. Different variations of this substrate-catalyst are being tested to optimize the growth. With a long molybdenum boat and a thin coating of the substrate-catalyst, almost one-half gram of SWCNT can be produced in each experiment using the nanofurnace. The time for purge-growth-cooling for one synthesis experiment is about four hours. The purification process including acid treatment, thermal annealing and washing takes about one day. Therefore, having both synthesis and processing running simultaneously, about one gram per day of SWCNT manufacturing may be possible. Using a thicker layer of catalyst and a longer boat could increase the yield, but this procedure mentioned is easy to conduct without using dangerous acids, and produces research grade nanotubes. Building smart materials requires a significant amount of nanotubes for sample preparation and the furnace is useful for producing the nanotubes, but the greatest utility of the furnace is to try new growth experiments to improve nanotube yield, length, and to try to control the chirality of the nanotubes. A large number of trial and error experiments are possible and required to optimize nanotube synthesis.

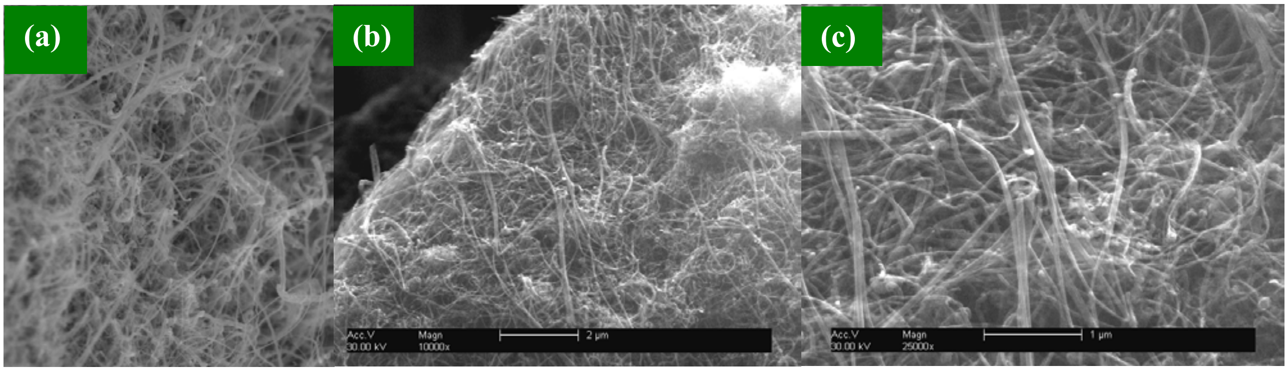

Figure 3. Bulk nanotube growth using a powder substrate and catalyst in a boat; (a) growth of SWCNT using the UC recipe for growth; (b) purified carbon nanotubes in ropes; (c) purified nanotubes/ropes close up.

4. RAMAN SPECTROSCOPY CHARACTERIZATION

The Raman technique is used in qualitative and quantitative analysis of carbon nanotubes. When a beam of light traverses a dust-free, transparent sample of a chemical compound, a small fraction of the light emerges in directions other than that of the incident (incoming) beam. Most of this scattered light is of unchanged wavelength. A small part, however, has wavelengths different from that of the incident light; its presence is a result of the Raman effect. The

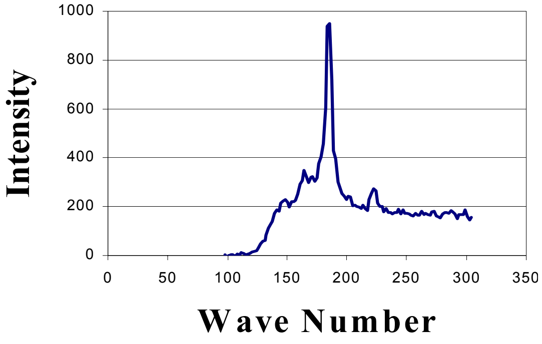

Figure 4. CNT Raman spectra
(A. Miskin, S. Jain, R.Gilliland).

pattern of the Raman lines is characteristic of the particular molecular species, and its intensity is proportional to the number of scattering molecules in the path of the light, or an indirect measure of the density of the respective species. Resonance peaks are also observed in the spectrum, which symbolize the presence of a particular specie type in abundance. In this analysis only wave numbers 0-300 (cm^{-1}) are considered for calculation of diameters. To estimate the electronic properties of nanotubes (i.e., whether nanotubes are metallic, semi - conducting or non-metallic), the wave number of interest must lie between 1400-1700 (cm^{-1}). Also if the light excitation energy is between 1.7 to1.9 eV, and resonance is observed in the 1400-1700 cm^{-1} wave number zone, it is an indication of metallic nanotubes. If the light excitation energy is above 2.2eV or below 1.5eV, and resonance peaks are observed in the 1400-1700cm^{-1} wave number zone, it is an indication of semi-conducting nanotubes. The relationship between diameter and resonance wave number is: Diameter (nm)=(238/ wave number (cm^{-1}))$^{1.07526}$. One of the Raman spectra is shown in Figure 4 which is a Raman spectra intensity-wave number graph. The mean wave number is the average value of resonance intensities observed between 0-300cm^{-1} in a sample. The mean diameter calculated is almost the same in the three experiments and is 1.3 nm. This seems typical as the diameter of nanotubes grown in CVD depends on the size of catalyst, and for these three experiments the same catalyst was used. The spectra resonance intensity magnitude starts increasing from sample 1 to 3, which also shows an increase in the relative density of nanotube growth. Hence we are able to produce more nanotubes by improving the process conditions. We observe a difference in resonant peak locations and their patterns in the region 300 to 1400cm^{-1}. Further analysis is needed to interpret the significance of this zone. The excitation energy of the laser sources in electro volts can be used to explore the zone 1400-1700 (cm^{-1}) and find variations in type of nanotubes produced (metallic or semi conducting) in the three samples.

Table 2. Numerical Data estimated from the Raman Spectra of SWCNT grown on a silicon substrate.

Experiment	**Resonance wave no (cm^{-1})**	**Intensity**	**Mean wave no (cm^{-1})**	**Diameter (nm)**
1-Std.	192.684	56.96	187.414	1.29
2-Modified	183.9018	600.377	180.385	1.35
3-Modified	169.8316	650.577	180.219	1.35

5. POLYMER NANOCOMPOSITES APPLICATION

Polymer nanocomposties can be produced by loading the resin with different weight percentages of nanotubes. In producing polymer nanocomposites the dispersion and bonding of the nanotubes to the matrix is the critical issue. To improve the dispersion and interfacial bonding between the resin and the nanotubes, the nanotubes are first dispersed in a monomer using a high-speed dremel tool. The nanotubes can then be coated with acrylic acid or another material in a plasma polymerization process. Another approach is to disperse the purified nanotubes in a surfactant and without coating. Nanocomposites are then made by mixing the carbon nanotubes in Epon 868 resin with a high-speed dremel tool at elevated temperature, and then curing with Epicure 3234. The main two problems encountered in this process are that the nanotubes tend to clump together when they are put in a resin or a matrix, and the nanotubes do not bond strongly enough to the matrix. The mixing can also damage the nanotubes. These effects result in degradation of the mechanical properties of the composite. For example, if carbon nanofibers are not functionalized, Figure 5 shows the pullout of nanofibers from an epoxy matrix. Composite samples containing different % by weight of the randomly aligned Carbon Nanofibers (CNF), the Pyrograf III type of different diameters have been cast. The CNF have diameters of 70 nm and 130 nm for two types and are similar to large MWCNT because of their concentric tubes, but the tubes are at a twenty degree angle to the fiber axis. If the nanofibers are coated to improve the dispersion and adhesion, about 30% improvement in the resulting elastic moduli of the nanocomposite materials is possible with 1 wt % loading of the nanofibers. The coating of nanofibers is shown in Figure 6. The properties can increase somewhat with greater weight percentages of nanofibers depending on the degree of dispersion and adhesion. Similar results are obtained when using SWCNT in epoxy, and when using the CNF in polystyrene.

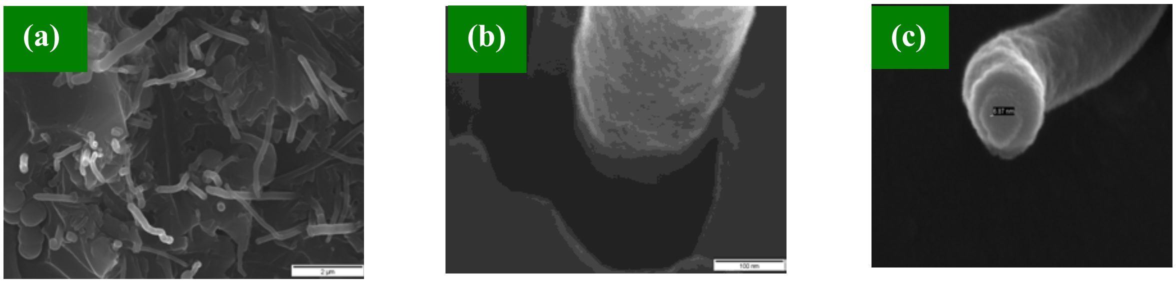

Figure 5. Uncoated nanofibers on the fracture plane of an epoxy polymer composite; (a) fiber pullout of matrix; (b) single fiber pullout; (c) fiber end showing amorphous carbon coating (images by Rob Gilliland using WPAFB SEM).

With higher percentages of nanotubes the properties are improved but are far below predicted properties using the rule of mixtures. To be cost effective, nanocomposites must provide a substantial improvement in properties. In this situation, the SWCNT have better properties, the MWCNT are easier to process and are lower cost, and the CNF are the lowest cost and are easier to process because of their larger diameter. Note in Figure 6(c) the dixie cup arrangement of the wall in which sections of tubes terminate. The nanocomposites can be a smart material because the electrical and mechanical properties can be tailored to meet specific applications.

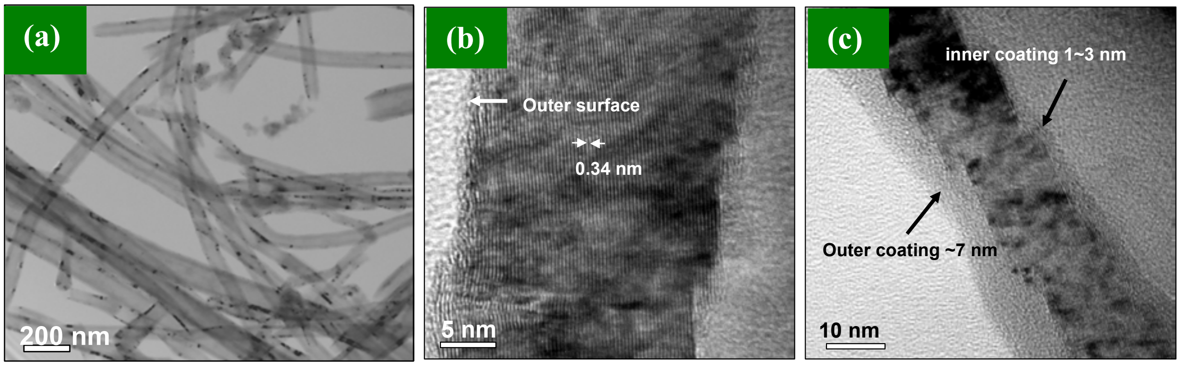

Figure 6. HRTEM images of Pyrograf III CNFs; (a) original uncoated PR-24-PS; (b) PR-24-HZ wall with inclined planes; (c) an ultrathin film of pyrrole coated on both outer and inner surfaces of the CNF (coating by D. Shi and T. He).

6. PIEZORESISTIVE SENSOR APPLICATION

Carbon nanotubes and their composites have a piezoresistive (electrical resistance changes with strain) response that is useful for monitoring loads and strains in composite structures. A CNT piezo-resistive load sensor and strain sensor are shown in Figure 7. The response of load sensor depends on the contact resistance between the composite and the electrodes. The response with a copper foil electrode in contact with the composite is shown in Figure 7(a). A transverse load was applied on this sensor and the resistance was measured using a multimeter. The initial part of the curve can be mostly removed by using a conductive epoxy to bond the electrode to the composite. It was observed that the resistance decreased with an increase in the load applied up to a certain value. The decrease in the resistance with an increase in the load can be used for sensing variations in load for structures. The slope of the later part of the curve can be tailored based on the percent of nanotubes in the epoxy. The results for compressive loading in which resistance decreases with loading may be the result of pushing the nanotubes closer together and improving the contact in the epoxy matrix and also because the thickness of the composite which is the distance between the electrodes, decreases with increasing load. Figure 7(b) shows the strain response of the SWNT film sensor with respect to the displacement of a structure. The response is quite linear but the sensitivity should be improved by using a smaller size sensor.

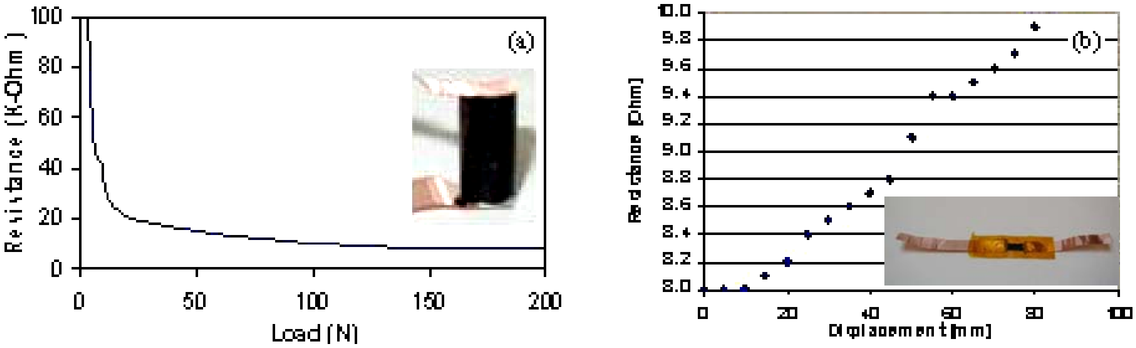

Figure 7. Piezo-resistivity of CNT; (a) Compressive piezo-resistance of a 5% random SWNT-epoxy load cylinder, (b) Strain response of SWNT film sensor (testing by P. Kang).

7. ELECTROCHEMICAL ACTUATOR APPLICATION

Different processes are being developed for making carbon nanotube and nanofiber actuators and sensors. In one approach, SWCNT are dispersed in N-N Dimethylformamide using a high-speed rotary tool and then aligned in a rectangular mold made of Teflon. A shear wiping action is used to try to align the nanotubes. Layer by layer the solvent is applied and evaporated. This slow process produces a somewhat aligned paper of 100% SWCNT. A thin layer of conductive epoxy is placed on one side of the paper and a wire is bonded to one end. This actuator is placed in an electrolyte (1M NaCl) and driven by a function generator with low voltage actuation on the order of volts. This actuator vibrates in the electrolyte at small amplitudes up to 1 mm at frequencies up to 15 Hz. Possible applications include actuation of anything operating in a liquid environment, and extension to the morphing of dry structures using an encapsulated electrolyte or dry electrolyte. The actuator can also act as a flow sensor by being connected to an oscilloscope. Fluid flow over the nanotube paper produces a peak voltage of 10 millivolts across a 1 M-ohm resistor.

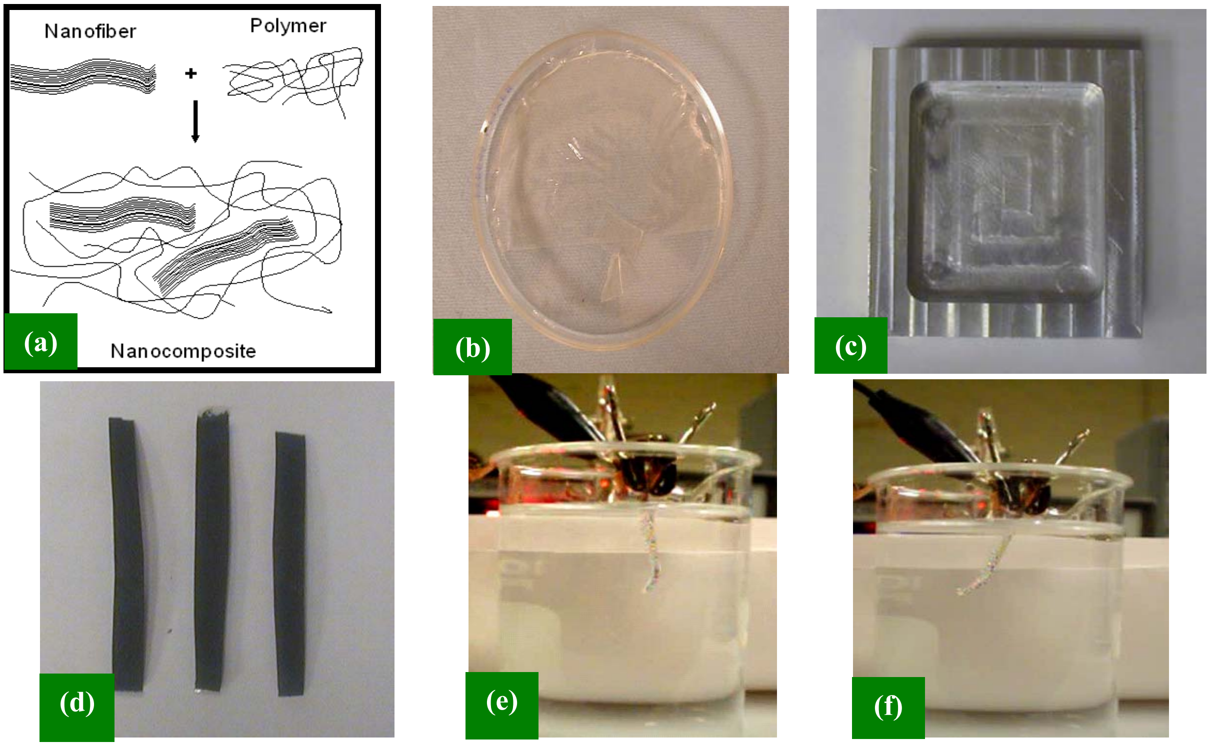

Figure 8. Processing of the CNF-Composite Material; (a) the CNF in a polymer matrix, (b) a gel electrolyte, (c) mold for casting CNF-Composite beams, (d) CNF-Composite strips, (e) CNF-Composite in NaCl no voltage, and (f) actuation with 20 volts DC applied (experiments by Y. Yeo-Heung, A. Miskin).

We are also developing for the first time CNF (Carbon Nanofiber [24]) - PMMA (Poly Methylmethacrylate) composites for electrochemical actuation, which is tested in both wet and dry solid electrolyte environments. A combination of solvent casting and melt mixing is used to disperse CNF materials in PMMA. Figure 8 shows different solid polymer electrolyte composite structures, prepared from PMMA, $LiBF_4$, PC (Propylene Carbonate), and ACN (Acetonitrile) by the solution casting method. Ion conductivity studies are carried out to characterize produced SPE. Comparing to SWNT buckpaper actuator as described in other works, larger force with smaller strain is produced using the CNF-SPE material, and higher voltage, about 20 volt peak, is needed to control it. Because the actuator may become the structural material, the CNF-PMMA composite actuator can be utilized for structural applications which make use of smart materials.

8. CONCLUSIONS

Building multifunctional materials that are strong and smart by using carbon nanotubes has been discussed, and some initial results have been presented. There are significant problems including dispersion and adhesion of nanotubes to the matrix material that still need to be overcome to commercialize the applications. Improved processing (both synthesis and dispersion) and material characterization techniques at reduced cost would generate many applications for multifunctional nanocomposite smart materials.

ACKNOWLEDGMENT

In order to perform this nanowork, the authors received and gratefully acknowledge the assistance from many different people. These include; David Burton of Pyrograph Inc., Thomas Pitstick from Carbon Nanotechnologies Inc., Dennis Adderton of FirstNano Inc., WPAFB for use of the SEM and Raman Facilities, and Don Bailey of the Ohio Aerospace Institute and Robert Bianco of Goodrich Corp. for technical suggestions to improve the nanocomposite processing.

REFERENCES

1. Exceptionally High Young's modulus observed from individual carbon nanotubes, Nature, 1996;381:680-7.
2. Erik T. Thostenson, Zhifeng Ren, Tsu Wei Chou, Composite Science and Technology, 1899-1912, Advances in the Science and Technology of Carbon Nanotubes and their composites: a review.
3. Iijima, S. Nature 1991, 354,56
4. Dresselhaus, M.S.,Science of Fullerences and Carbon Nanotubes, Academic Press, San Diago 1996.
5. Xie S,Li W, Pan Z, Chang B, Sun L. Mechanical and Physical properties of Carbon Nanotubes. Journal of Physics and Chemistry of solids, 2000; 61(7): 1153-8.
6. Pulickel M Ajayan, Otto Z. Zhou, Applications of Carbon Nanotubes, http://www.rpi.edu/locker/38/001238/publications/Ajayan_Zhou10800391.pdf.
7. R. H. Baughman, C. Cui, A. A. Zakhidov, Z. Iqbal, *et al.*, "Carbon Nanotube Actuators," *Science*, 284, 1340-1344 (1999).
8. NATURE , VOL 423, 12 JUNE 2003, www.nature.com/nature, *Super-tough carbon-nanotube fibres*, Alan B. Dalton, Steve Collins, Edgar Muñoz, Joselito M. Razal, Von Howard Ebron, John P. Ferraris, Jonathan N. Coleman, Bog G. Kim, Ray H. Baughman.
9. Virginia A. Davis, Lars M. Ericson, Rajesh Saini, Ramesh Sivarajan , R.H. Hauge, Richard E. Smalley, Matteo Pasquali, 2001, "Rheology, Phase Behavior, and Fiber Spinning of Carbon Nanotube Dispersions," AIChe Annual Meeting.
10. News.Nano.Apex, U.T. Dallas Scientists spin carbon nanotube fibers with record strength and toughness, June, 2003.
11. Wang, X., Drew, C., Lee, S., Senecal, K.J., Kumar, J., Samuelson, L.A., Electrospun Nanofibrous Membranes for Highly Sensitive Optical Sensors, Nanoletters, vol 2, no 11, 2002.
12. H. Liu, H. T. Cheng, F. L. Cong, G. Su, *et al.*, "Synthesis of Macroscopically Long Ropes of Well-Aligned Single-Walled Carbon Nanotubes," *Advanced Materials*, 12, 1190-1192 (2000).
13. Ge M, Sattler K Bundles of Carbon Nanotubes by Gas Phase Growth, Applied Physics Letters, 1994; 64(6): 710-1
14. Zhang Y Iijima, Formation of Single Walled Carbon Nanotube by Laser Ablation at low temperature, Applied Physics Letter, 1999,3087-9
15. Shi Z Lian, Liao F.H, Large Scale synthesis of Single Walled Nanotube by Arc Discharge method, Journal of physics and chemistry of solids 2000; 61(7): 1031-6
16. Alan M. Cassell, J. Raymakers, Jing Kong, J. Phys. Chem.B 1999, 103, 6484-6492. Large Scale CVD Synthesis of Single Walled Carbon Nanotubes
17. Jing Kong, Hyongsok T. Soh, Alan M Cassell, Calvin F. Quate, Nature, Vol 395,29 Oct, Synthesis of individual

single walled carbon nanotubes on patterned silicon wafers.

18. H.W. Zhu, C.L.Xu, P.M.Ajayan, 3 May, 2002, Vol 296, Science, Direct Synthesis of Long Single Walled Carbon Nanotube Strands
19. Nikolaev P Bronikowski, MJ, Brandley, Chemical Physics Letters, Gas Phase Catalytic growth of Single walled carbon nanotubes from carbon monoxide, 1999; 313 (1-2): 91-7
20. Application Note: Preparation of Carbon Nanotube Catalyst, FirstNano, Santa Barbara, California 93111.
21. Application Note: Synthesis of Carbon Nanotubes with the Easy Tube System, FirstNano, Santa Barbara, California 93111
22. FirstNano Inc., Manufacturer of EasyTube Nanofurnace, www.firstnano.com.
23. Carbon Nanotechnologies, Inc., www.cnanotech.com.
24. Applied Sciences Inc., www.apsci.com.