Multifunctional smart composites with integrated carbon nanotube yarn and sheet

Devika Chauhan, Guangfeng Hou, Vianessa Ng, Sumeet Chaudhary, Michael Paine, et al.

Devika Chauhan, Guangfeng Hou, Vianessa Ng, Sumeet Chaudhary, Michael Paine, Khwaja Moinuddin, Massoud Rabiee, Marc Cahay, Nicholas Lalley, Vesselin Shanov, David Mast, Yijun Liu, Zhangzhang Yin, Yi Song, Mark Schulz, "Multifunctional smart composites with integrated carbon nanotube yarn and sheet," Proc. SPIE 10172, A Tribute Conference Honoring Daniel Inman, 1017205 (10 April 2017); doi: 10.1117/12.2258563

Event: SPIE Smart Structures and Materials + Nondestructive Evaluation and Health Monitoring, 2017, Portland, Oregon, United States

Multifunctional Smart Composites with Integrated Carbon Nanotube Yarn and Sheet

Devika Chauhan[a], Guangfeng Hou[b], Vianessa Ng[b], Sumeet Chaudhary[b], Michael Paine[b], Khwaja Moinuddin[b], Massoud Rabiee[d], Marc Cahay[d], Nicholas Lalley[d], Vesselin Shanov[b], David Mast[c], Yijun Liu[b], Zhangzhang Yin[b], Yi Song[b], Mark Schulz[b*]

[a] Dept. of Aerospace Engineering and Engineering Mechanics, University of Cincinnati, OH 45221, USA; [b] Dept. of Mechanical and Materials Engineering, University of Cincinnati, OH 45221, USA; [c] Dept. of Physics, University of Cincinnati, OH 45221, USA; [d] Dept. of Computer and Electrical Engineering, University of Cincinnati, OH 45221, USA

ABSTRACT

Multifunctional smart composites (MSCs) are materials that combine the good electrical and thermal conductivity, high tensile and shear strength, good impact toughness, and high stiffness properties of metals; the light weight and corrosion resistance properties of composites; and the sensing or actuation properties of smart materials. The basic concept for MSCs was first conceived by Daniel Inman and others about 25 years ago. Current laminated carbon and glass fiber polymeric composite materials have high tensile strength and are light in weight, but they still lack good electrical and thermal conductivity, and they are sensitive to delamination. Carbon nanotube yarn and sheets are lightweight, electrically and thermally conductive materials that can be integrated into laminated composite materials to form MSCs. This paper describes the manufacturing of high quality carbon nanotube yarn and sheet used to form MSCs, and integrating the nanotube yarn and sheet into composites at low volume fractions. Various up and coming technical applications of MSCs are discussed including composite toughening for impact and delamination resistance; structural health monitoring; and structural power conduction. The global carbon nanotube overall market size is estimated to grow from $2 Billion in 2015 to $5 Billion by 2020 at a CAGR of 20%. Nanotube yarn and sheet products are predicted to be used in aircraft, wind machines, automobiles, electric machines, textiles, acoustic attenuators, light absorption, electrical wire, sporting equipment, tires, athletic apparel, thermoelectric devices, biomedical devices, lightweight transformers, and electromagnets. In the future, due to the high maximum current density of nanotube conductors, nanotube electromagnetic devices may also become competitive with traditional smart materials in terms of power density.

Keywords: Multifunctional; smart; composite; carbon nanotube sheet and yarn

1. INTRODUCTION

Laminated carbon and glass fiber polymeric composite materials have high tensile strength and are light in weight, but lack metal-like electrical and thermal conductivity, and are sensitive to damage, especially delamination damage. Multifunctional smart composites are a new material that is a combination of carbon nanotube (CNT) sheet and yarn and conventional fiber composites. This multifunctional material has good electrical and thermal conductivity, can be used for strain sensing, has high tensile and shear strength, and high stiffness, and is lightweight. This presentation describes manufacturing multifunctional smart polymeric composites and presents some of the properties of this material.

1.1 Manufacturing Carbon Nanotube Sheet and Yarn

Carbon Nanotubes are manufactured in a floating catalyst method at the Nanoworld Laboratory at the University of Cincinnati. Argon and ferrocene are injected in the front end of the furnace tube as shown in Fig. 1. Decomposition of ferrocene forms an iron catalyst. The catalyst, passing through the high temperature zone, nucleates CNT growth. At the outlet end of the furnace tube, the CNT assemble into an aerogel-like sock Error! Bookmark not defined..

* Corresponding author. Tel: (513) 556-4132; email: Mark.J.Schulz@uc.edu.

A Tribute Conference Honoring Daniel Inman, edited by Donald J. Leo, Pablo A. Tarazaga, Proc. of SPIE Vol. 10172, 1017205 · © 2017 SPIE · CCC code: 0277-786X/17/$18 · doi: 10.1117/12.2258563

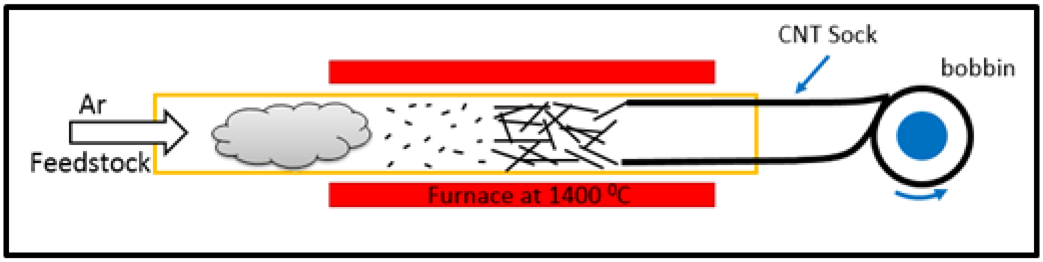


Figure 1. Schematic of catalyst floating manufacturing of CNT sheet.

This aerogel-like sock is collected on a winding Teflon drum (Fig. 2) to form CNT sheet. Acetone is used to densify the CNT sheet. The Teflon drum is cut and the sheet is unwrapped. Thickness of the sheet is controlled by the number of revolutions of the drum during the synthesis process. Yarn is formed by pulling the hydrophobic sock through a water bath which collapses the sock into a ribbon which is wound onto the drum. The ribbon is subsequently drawn and twisted to form yarn with a controlled number of turns/length.

Figure 2. CNT sock being wrapped on a Teflon drum.

2. POST PROCESSING OF CARBON NANOTUBE SHEET

Individual CNTs have excellent physical properties in terms of electrical conductivity and strength. The strength of individual single walled carbon nanotubes ranges from 11GPa -63 GPa [2] and the electrical conductivity is as high as 10^6 S/cm[3]. The properties of multi-wall CNTs are lower than single wall CNTs. In bulk materials that are assemblages of nanotubes, such as CNT sheet and yarn, these physical properties are greatly decreased. Extensive research is being conducted around the world to try to bring the physical properties of the individual CNTs to bulk material. The strength of CNT sheet and yarn is limited by the weak van der Waal's forces acting between CNT, and on friction forces in the twisted yarn. The reduced electrical conductivity of the bulk CNT sheet and yarn are due to the many contact points between carbon nanotubes which are scattering sites or resistances for electrons. Defects in the carbon nanotubes also reduce the strength and electrical conductivity compared to perfect nanotubes. Chemical and physical post processing of the as-produced CNT sheet are performed as one approach to improve the properties of CNT assemblages. This paper will discuss only the physical post processing of the CNT sheet which does not affect the chemistry of the nanotubes. Physical post-processing is comprised of stretching and pressure compression of the CNT sheet which improves the packing and alignment of the CNTs in the bulk sheet, and increases the number of contact points between CNTs.

2.1 Stretching CNT sheet

CNT sheets are stretched in one direction to improve their alignment and provide parallel paths for current flow. When CNTs are arranged and packed in parallel to each other they act as parallel conductors which increases electrical conductivity because the cross-sectional area of the conductor is decreased. Also, the material density is increased. Stretching CNT improves the tensile strength and electrical conductivity in the stretching direction, and may reduce the properties in the transverse in-plane direction. In Fig. 3, it can be seen in the scanning electron microscope (SEM) images that there is an improvement of directional alignment among CNT strands.

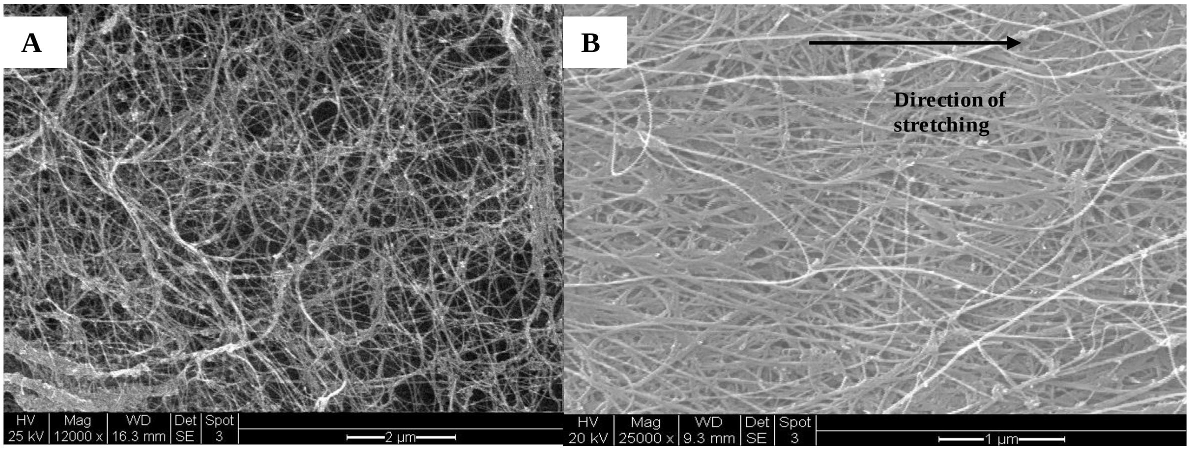


Figure 3. SEM image of CNT sheet: A) As produced; B) Stretched CNT sheet.

2.2 Densification of CNT sheet

The CNT sheet is densified by rolling the CNT sheet under high pressure in a rolling mill. The applied high pressure helps bring the CNT strands close to each other, as can be seen in Fig. 4. The densification increases the contact points among the CNT strands and thus increases the tensile strength and electrical conductivity of the CNT sheet. Densification by evaporation of a solvent (capillary forces bring the CNTs together) from the CNT sheet is also performed.

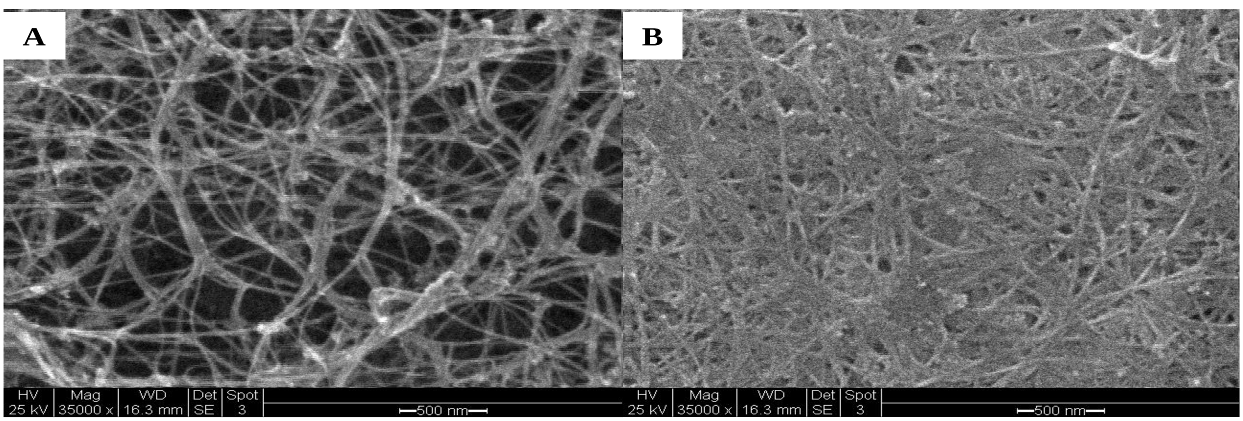


Figure 4. SEM image of CNT sheet: A) As produced; B) Pressure densified CNT sheet.

3. MATERIAL CHARACTERIZATION AND TESTING

Careful characterization and testing are performed to improve the electrical conductivity and tensile strength of the CNT sheet for applications like electrically conductive fiber reinforced composites and structural health motoring. In order to achieve these goals, tests are performed one after another. Characterization of the physical properties of CNT sheet was performed before integrating the sheet into fiber reinforced composite laminates to form smart structures.

3.1 Characterization of CNT Sheet

CNT bulk materials such as sheet and yarn lack the high physical properties of individual CNTs. Therefore, it is essential to evaluate and compare the physical properties of pristine CNT sheet and post processed CNT sheet. This helps to understand and optimize the many parameters in the post processing methods. Tensile testing of the CNT sheet was conducted using an Instron 5900 tensile test machine. Electrical testing of the resistivity of the pristine CNT sheet and the post processed CNT sheet was performed using a four probe LR700 analyzer, or a two-probe tester. Resistivity was computed by applying a correction factor per the Van der Pauw method[4].

For the tensile testing of the pristine CNT sheet and post processed CNT sheet, samples were 40mm long and 2mm wide. The test samples were fixed on a test frame as shown in Fig. 5A. The test was carried out with displacement control at a displacement rate of 1mm per minute. The thickness of the CNT sheet was measured with the help of a bench-top SEM, as in Fig. 5B. After the testing, the results were analyzed and the failure surface was observed.

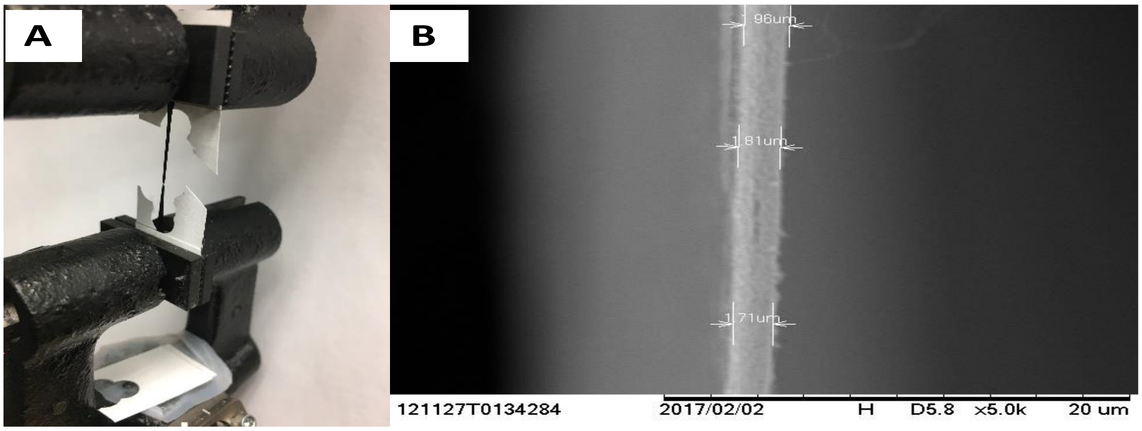


Figure 5. Tensile testing set-up: A) CNT Sheet test samples attached to test frame; B) Thickness of CNT sheet is about 1-2 microns.

The tensile test showed 650% improvement of the mean tensile stress at break for post-processed CNT sheet (from 13 MPa for a pristine sheet up to 100 MPa for the post-processed CNT sheet). Also, there is 50% reduction in tensile strain at failure for post-processed CNT sheet compared to pristine sheet. Stress-strain results are shown in Fig. 6.

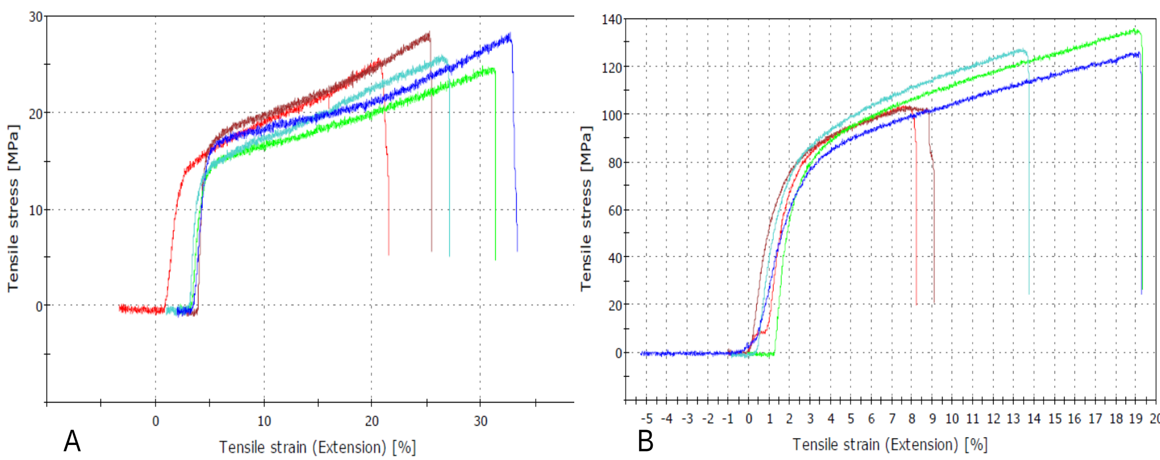


Figure 6. Tensile test results: A) for pristine CNT sheet; B) for post-processed CNT sheet.

Additionally, the electrical characterization of the CNT sheet showed an improvement in electrical conductivity of 50% with post-processing of CNT sheet. The post-processing parameters are not optimized yet and much greater improvement in properties is expected. Also, the properties increase with decreasing thickness of the sheet. Moreover, the electrical properties depend on the synthesis conditions (temperature, flow rate, dwell time) and sheet with good electrical conductivity (of the order of 10^4 S/cm) can be manufactured but the yield of the process decreases.

3.2 Manufacturing Composite Laminates

Commercially available carbon fiber composite laminates have low electrical conductivity and fiberglass composites are electrically insulating. Electrical conductivity provides added functionality to the composite. CNT sheets were integrated between the plies to increase the conductivity in the plane of the laminates. The manufactured CNT sheet integrated composite laminates were used to carry out tests for fracture toughness and electrical conductivity. The composite laminates were manufactured by interleaving CNT sheet in-between Glass fiber plies. Aero Epoxy was used as an adhesive. The laminates were then cured in a hot press at elevated temperature and pressure as per instruction for the Aero-Epoxy curing cycle. After four hours of curing, the laminates were cut in a Diamond Abrasion Cutting machine to make test coupons.

3.3 Short Beam Shear (SBS) Testing

A12-ply composite panel was cut along the boundary between the CNT sheet and the fiberglass as in Fig. 7A. The two pieces were cut separately into 0.5”×0.25” prismatic test coupons for short beam shear testing. Short beam shear testing was performed using an Instron 4468 machine with the loading rate of 0.02”/min (Fig. 7B). The distance between support pins was 8 mm. Table 1 lists the material dimension and properties.

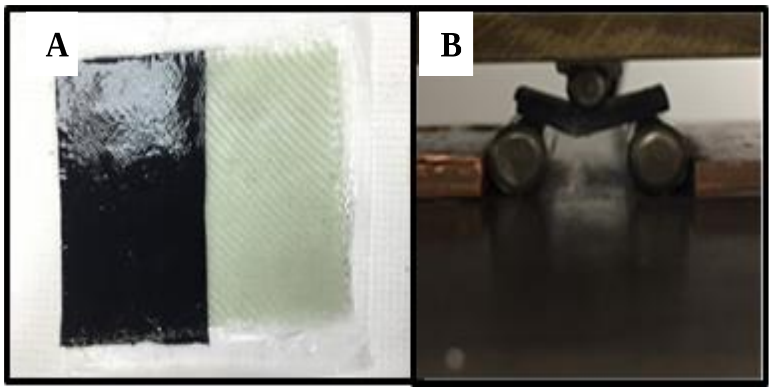


Figure 7. Composite strength testing: A) Fiberglass ply and CNT sheet lay-up; B) Short beam shear test.

Table 1. Interlaminar Shear Strength from the Short Beam Shear (SBS) Test.

Composite Configuration	Width (mm)	Thickness (mm)	SBS Strength (MPa)	Mean SBS Strength (MPa)	STDEV	Increase of SBS Strength (%)
12-ply FG 1	5.05	2.26	42.5	39.2	3.3	0
12-ply FG 2	5.27	2.04	34.6			
12-ply FG 3	5.18	2.21	39.5			
12-ply FG 4	5.21	2.11	40			
12-ply FG&CNT Sheet 1	5.27	2.43	43.8	42.7	2.2	9.1
12-ply FG&CNT Sheet 2	5.27	2.29	39.5			
12-ply FG&CNT Sheet 3	5.31	2.46	44.6			
12-ply FG&CNT Sheet 4	5.17	2.39	42.9			

From Table 1, the interlaminar shear strength of the CNT sheet reinforced laminated composites increased 9% compared to the laminated composite without CNT sheet reinforcement. Adding CNT sheet into laminated composites did not reduce load transfer between the intermediate glass fibers and brittle resin. Fig. 8 shows the short beam shear test curves for all the test coupons. The CNT sheet must be thin or the ILSS will decrease. Another approach is being investigated to greatly increase the ILSS of composites[6] when thicker CNT sheets are used.

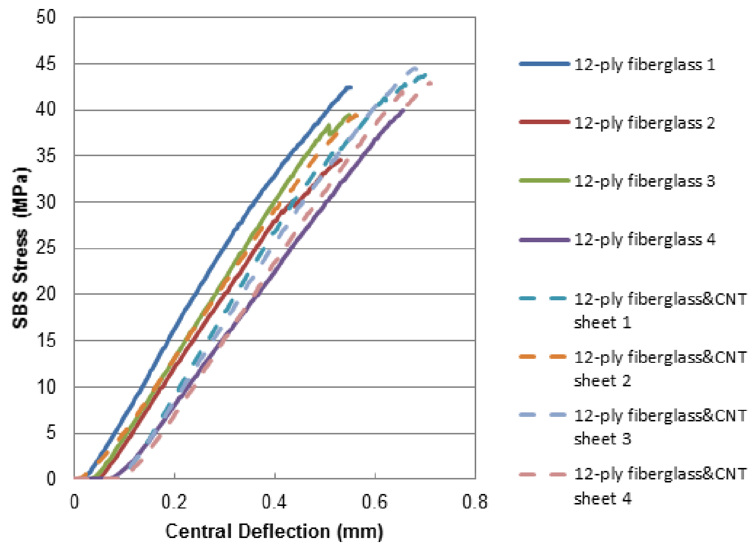


Figure 8. SBS results for 12-ply fiberglass composites with/without CNT sheet reinforcement.

3.4 Electrical Conductivity Measurement

The other test conducted on composite laminates was to measure the electrical conductivity by the two probe method. Voltage and current values are used in the basic equation (1) to find the conductivity of the laminates:

$$\sigma = \frac{L}{Rtw}. \tag{1}$$

Here R is the resistance, L is the length, t is thickness and w is the width of the sample. The in-plane electrical conductivity of the CNT sheet reinforcement measured was 243 S/cm compared to the non-conductive fiberglass laminates.

4. STRUCTURAL HEALTH MONITORING OF COMPOSITES

Carbon nanotube sheet is a promising material for structural heath monitoring (SHM) in fiber reinforced composite structures. Conductive CNT sheet can be used as a sensor for damage/strain sensing in the structure. For this application, three-ply glass fiber laminates interleaved with CNT sheet along the center section of the laminate were manufactured. The composite laminate was mounted on the test fixture equipped with a round head pendulum impactor of weight 6 lbs. and connected to Craftsman 82334 Multi-meter. Initial resistance reading of the nano-composite laminate measured was 11.7 Ohms. With an initial impact of energy 0.67 J, there was an increase in resistance of 1.7% in the structure. When an impact energy of 1.69 J was applied in a second impact, there was an additional increase in resistance of 2.5% in the structure. The nano-composite was impacted with an increasing impact energy of 3.38 J, 4.75 J, 6.77 J and 23 J consecutively. As a result, the structure showed an increase in resistance of 7.3%, 4.5 %, 1.4% and 29% respectively relative to the resistance of the preceding impacts (Fig. 9).

After consecutive impacts, the resistance of the carbon nanotube-glass fiber composite structure increased to 18 ohms showing an overall increase of 54% due to damage of the interleaved CNT sheet compared to the undamaged laminate. About 1/3 of the CNT sheet width is removed in the damaged area (hole) due to a 24 J impact, and multiple prior smaller impacts. A damage indicator (D) predicts 35% damage at the 24 J impact (R is the resistance of the CNT sheet in the healthy or damaged composite structure).

$$D = \left(1 - \frac{R_{healthy}}{R_{damaged}}\right)100 \text{ or } D = \left(1 - \frac{11.7}{18}\right)100 = 35\%. \tag{2}$$

CNT yarn is also used for damage detection in composites[5]. Various configurations including multiplexing over many sensors are available. The advantage of the sensor sheet is damage can be detected over larger areas as compared to using CNT yarn as the sensor, or other types of sensors. The limitation of using the CNT sensor sheet is the sensitivity to small damage is reduced, and the damage is located only within the area region of the sensor.

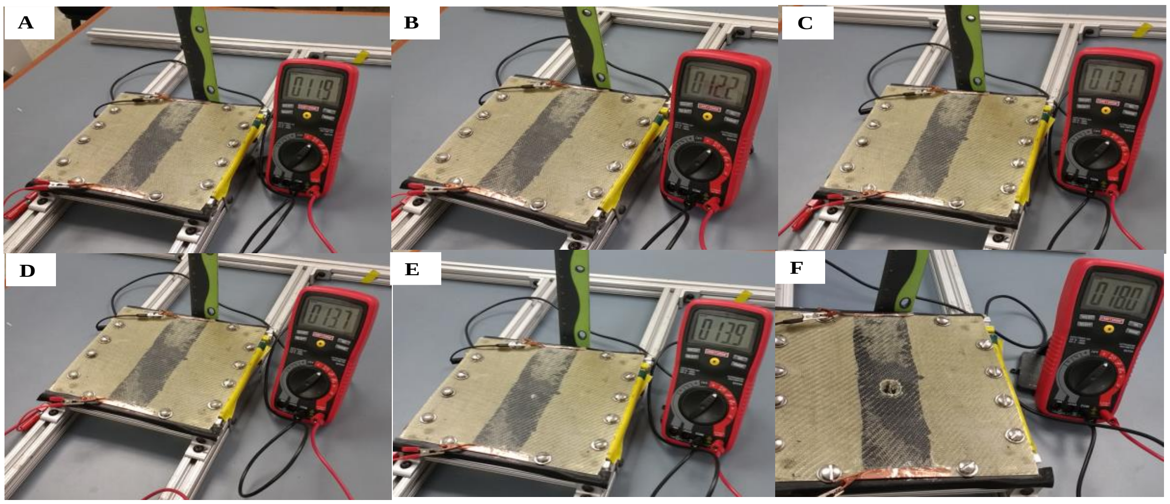


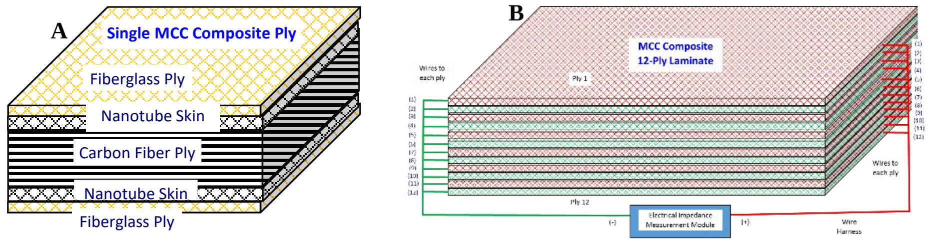
Figure 9. Increase in resistance of the structure with increase in impact energy: A) Impact energy 0.67 J; B) Impact energy1.69 J; C) Impact energy 3.38 J; D) Impact energy 4.75 J; E) Impact energy 6.77 J; F) Impact energy 23 J.

5. STRUCTURAL POWER CONDUCTION

Structural wire (SW) is a new concept where a multifunctional composite material is used to carry load and also to carry electrical signals or current. Structural wire is formed by integrating carbon nanotube sheet with electrical insulation in between carbon fiber plies in a laminated polymeric composite. The CNT sheet is the power line. The carbon fiber plies in the structure are the return and ground lines. Thus the structure is also the wire. The CNT sheet optionally may be integrated with Cu material to increase its conductivity. Thus the weight of electrical wires is reduced in vehicles. The space required for electrical wires also becomes available for other uses. Reducing the weight of vehicles is possible by reducing the use of copper wire and the wiring harnesses. As an example, a typical carbon fiber laminated composite may have 12 plies. The structural composite is formed by inserting carbon nanotube plies in between the carbon fiber plies. Thus a composite with twelve plies of carbon fiber will have 11 plies of carbon nanotube conductor. This provides 11 wires in the structural material in any cross-section. Spatially in plane there can be multiple stacks of wires side by side. Thus the structure is actually the wire harness and the wires.

SW is designed to ensure integrity of the structure. In particular, the SW must not significantly reduce the structural properties such as interlaminar shear strength (ILSS). The CNT layers increase the thermal conductivity and maintain the ILSS of the material. The tensile strength of the composite is reduced by a small amount. The SW must be designed to carry the desired type of signal. Control signals can be carried by smaller size wires. Power conduction wires are larger. Insulation will depend on the voltage required. Higher voltage will reduce I^2R loss. CNT sheet properties can be controlled to some degree. Nanoparticles can also be added in the synthesis process into the CNT sock before it exits the reactor and is rolled into sheet. The nanoparticles may improve the electrical or magnetic properties of the sheet[6].

SW is formed using CNT sheet or yarn. The nanotube sock is densified and drawn and optionally twisted as it exits the reactor. SW can also be formed by integrating carbon fiber layers such as IM7 or carbon fabric with the carbon nanotube layers. Each layer in a composite is formed using the SW ply with the nanotube sheets acting as skins, Fig-10A. This structural material can be used for electrical conduction and sensing. The in-plane electrical impedance of the laminate ($Z_{i,j}$) is modeled as shown in Fig-10B,C.



C

$$Z = \begin{bmatrix} z_{11} & z_{12} & z_{13} & \cdots & z_{1n} \\ & z_{22} & z_{23} & \cdots & z_{2n} \\ & & z_{33} & \cdots & z_{3n} \\ & symm & & \ddots & \vdots \\ & & & & z_{nn} \end{bmatrix}$$

Figure 10. Construction of SW: (a) single ply SW; (b) a 12 ply SW laminate with 12 electrical circuits. The structure becomes the wiring harness and wires; (c) The electrical impedance will be modeled.

Fabrication and testing of SW as an electrical conductor is illustrated in Fig-11a, b. An IM7 carbon fiber ply with two CNT sheet skins sandwiched between two fiberglass prepreg plies is used as the SW. The SW is placed in series in an electrical circuit to operate a power tool without significant heating of the SW, Fig-11b. The IR camera shows the SW is near room temperature and the resistive heating is small. Structural capacitors and lightning strike protection are other applications that can be considered.

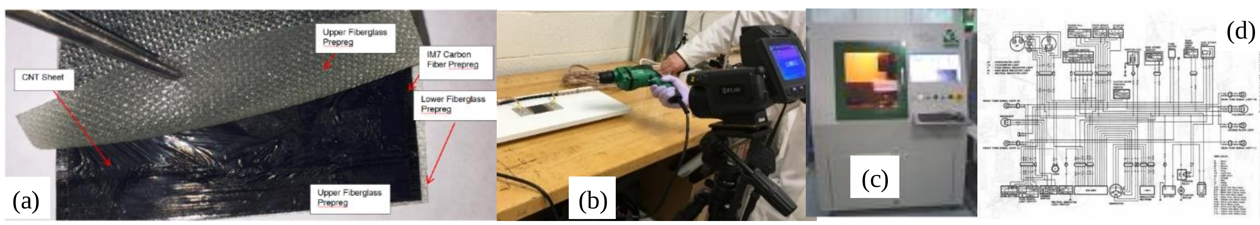


Figure 11. SW designed as a composite material: (a) IM7 carbon fiber ply with two CNT sheet skins sandwiched between two fiberglass prepreg plies; (b) The SW is used in an electrical circuit to operate a power tool without significant heating of the SW as shown by the IR camera; (c) CNT sheet can serve as a circuit board in additional to just a conductor. Wiring patterns can be formed in the sheet by laser burning out the CNT using the Oxford laser machining system, cutting cannot shear the nanotubes and provide a sharp edge.; (d) A wiring diagram that might be patterned into the SW in different layers using 3D laser machining. The wiring diagram can be downloaded to the laser machining system.

7. CONCLUSIONS

Carbon nanotube Sheet and yarn will be part of the future of smart structures. Moreover, Carbon nanotube integrated structures can be used for Structural wire, EMI shielding, Structural health monitoring, Lightning strike, and De-icing applications. With extensive research, all the mentioned application can be combined into one smart structure and help reduce weight by eliminating dozens of sensors, heaters, wires, and actuators added to structures. CNT sheet or yarn is well suited to form multi-purpose composites that provide load bearing capability, electrical conduction for lightning discharge, electromagnetic shielding, damage detection, and power conduction - all with the same material. Thus the composite is considered a Multifunctional Smart Composite (MSC). Actuation capability is in development and may rely on the use of CNT electromagnetic actuators rather than conventional smart materials like piezoelectric ceramics or shape memory alloys or polymers, or other smart materials. Our vision is the structure is also the actuator, i.e. the structure carries load and is an electromagnetic actuator. Nanoizing composites is just an extension of the concept of smart structures started by Daniel Inman and others about 25 years ago.

ACKNOWLEDGMENT

This research was supported by the ONR Project *Carbon Nanotube Synthesis* with Program Manager Dr. Ignacio Perez; the Univ. of Cincinnati Education and Research Center Targeted Research Training program (UC ERC-TRT Program); the Univ. of Cincinnati Accelerator Program; and builds on other research projects supported from the NSF, Air Force, and ONR over the past 23 years.

REFERENCES

[1] Hou G, Su R, Wang A, Ng V, Li W, Song Y, Zhang L, Sundaram M, Shanov V, Mast D, et al. "The effect of a convection vortex on sock formation in the floating catalyst method for carbon nanotube synthesis," Carbon (New York) 102, 513-519 (2016).

[2] Ruoff RS, Yu M, Lourie O, Dyer MJ, Moloni K, Kelly TF,"Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load," SCIENCE 287, 637-639 (2000).

[3] Li Q, Li Y, Zhang X, Chikkannanavar SB, Zhao Y, Dangelewicz AM, Zheng L, Doorn SK, Jia Q, Peterson DE, et al. "Structure-dependent electrical properties of carbon nanotube fibers," Adv Mater 19, 3358-3363 (2007).

[4] Buehler MG, Thurber WR. "Measurement of the resistivity of a thin square sample with a square four-probe array," Solid-State Electronics 20(5), 403-406 (1977).

[5] Jandro L. Abot, Yi Song, Maruthi Sri Vatsavaya, Sandeep Medikonda, Zachary Kier, Chaminda Jayasinghe, Nathan Rooy, Vesselin N. Shanov, Mark J. Schulz. "Delamination detection with carbon nanotube thread in self-sensing composite materials," Composites Science and Technology, Volume 70, Issue 7, July 2010, Pages 1113-1119.

[6] UC Provisional Patent Application, Manufacturing Nanotube Hybrid Sheet and Yarn by Gas Phase Assembly, Mark Schulz, Guangfeng Hou, Vianessa Ng, et al, February, 2017.