Carbon as Conductor: A Pragmatic View

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Abstract

Carbon nanotubes (CNT) have been touted as a game-changing material for medicine, microelectronics, and renewable energy. Moving beyond hype to product development, efforts at TE Connectivity (TEC) have focused on electromagnetic interference shielding and data transmission cables using commercially available CNT materials. With a tape format we have achieved greater than 50dB shielding effectiveness in GHz range; current CNT materials do not provide adequate shielding below 100 MHz. Data transmission cables made using a yarn format perform comparably to MIL-STD 1553. Termination is possible using standard techniques (e.g. crimping, soldering) without contact resistance issues due to the relatively high resistivity of the CNT formats. A key area of improvement is enhanced conductivity of the CNT macroscopic formats to enable both high speed and power applications, not currently possible with commercially available CNTs. Environmental, safety, and health concerns are non-trivial and we share our approach in this paper.

Keywords: carbon nanotube, shielding, center conductor, data transmission, environmental health and safety, termination, crimping, plating

Introduction

Low density carbon allotropes, like graphene and CNTs, have garnered significant attention from academia, government labs and industry as an enabling material for future technologies [1]. Applications proposed and/or under development utilizing these materials include composite structures for aviation, transparent conductors for consumer electronics, antennas, biochemical sensors, super capacitors, actuators ("artificial muscles") and ballistic protection. The Advanced Development Group within the Aerospace, Defense, and Marine Division at TE Connectivity is exploring the use of nanomaterials in three areas: (a) conductive composite enclosures, (b) chemical sensors, and (c) wire and cable. This paper summarizes recent efforts in using carbon nanotubes based materials in cable constructions.

The immediate driver for incorporation of CNT based materials in wire and cable is weight reduction. Consider an RG-58 coaxial cable; the weight of a standard copper construction is 38.8 g/m. Replacing the copper braid with CNT wrap reduces the weight to 11.5g/m. Replacing both the copper braid and center conductor with CNT tape and yarn, respectively, further reduces the weight to 7.3 g/m – a savings of eighty percent [2.] Such reductions translate to hundreds of pounds in an aircraft – for example, the F-35 military aircraft has approximately 15 miles of cable on each jet. Replacing copper shielding with CNT saves 1,180 pounds; all CNT cables would save 1,975 pounds.

1. Material Types and Test Methods

Commercially available CNT-based materials were used for substrate based testing and prototype builds; the materials and their form factors are summarized in Table 1, below:

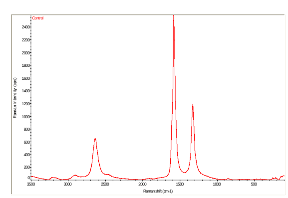
Table 1. Carbon Nanotube Commercial Materials

Format	Manufacturer	Application
Yarn	Nanocomp Technologies, Inc	Center conductor
Tape	Nanocomp Technologies, Inc	Shielding
Sheet	Buckeye Composites, Inc	Shielding
Fiber	Applied Nanostructured Solutions, Inc.	Shielding
Powder	Continental Carbon Nanotechnologies, Inc.	Shielding

The material was inspected using high-resolution scanning electron microscopy, Raman spectroscopy (comparison of the G and D bands to determine the number of walls in the tubes), and thermal gravimetric analysis (TGA) to determine the amount of residual catalyst and other impurities in the material. Most of the material comprised of few- or dual-wall carbon nanotubes with few impurities and residual catalyst in the single digits by weight.

Figure 1 part (a) shows the Raman spectra for the Nanocomp yarn; the standard Raman G and D band ratios are shown for dual and multi-walled CNTs, respectively in part (b.)

(a)



(b)

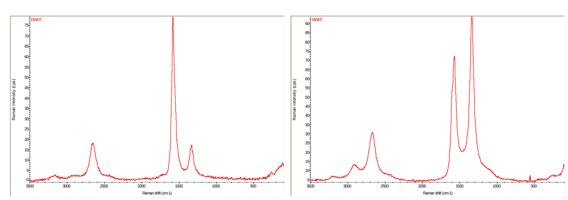


Figure 2. Raman spectroscopy of (a) Nanocomp Yarn and (b) Dual- (left) and Multi- (right) walled CNTs

TGA data of a sixty ply (24 AWG equivalent diameter) yarn is shown in Figure 2; slightly more than 92% of the material was loss at 896C suggesting catalyst contamination of roughly 8%.

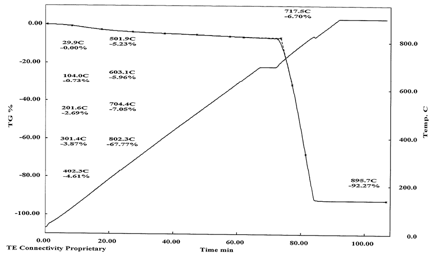


Figure 2. TGA analysis of 60-ply Nanocomp yarn

Each manufacturer's material was used for a high frequency (1 to 8 GHz) electromagnetic interference shielding effectiveness test. The experimental method used was an adaption of the ASTM D4935 procedure allowing the use of a smaller diameter substrate (3 cm.) CCNI nanotubes were used to create two substrates for testing: a spray coated film on a polymer substrate and an all-CNT "buckypaper" created by a vacuum filtration onto a support.

The nanomaterials results were compared to the standard materials listed in Table 2:

Table 2. Comparison Materials

Format	Manufacturer/Product	Material
Braid	TEC	Copper
Braid	GlenAir/Amberstrand®	Composite
Sheet	Swift Textile Metalizing	Metal-plated polymer
Sheet	Metal Textiles Corporation	Metal-plated polymer
Sheet	Graf-X®	Graphite

In Table 3, the areal density (g/m^2) of the each material and its shielding effectiveness (dB) is listed at 4 GHz:

Table 3. Shielding Effectiveness at 4 GHz

Sample	Areal Density (g/m^2)	SE (dB) at 4GHz
Metallic Over-Braid	**3500**	**50**
Amberstrand®	585	40
Graf-X®	538.2	70
STM Ag/Nylon Loop	125.5	60
STM NiAg/Nylon Tafetta	78	50
MTC CuNi/Polyester	68	68
Nanocomp Sheet (2 layers)	**40**	**52**
CCNI Buckypaper	35	58
Nanocomp sheet (1 layer)	19	44
CCNI Spray coated CNT	0.8	27

The nanomaterials show solid high frequency shielding effective performance at low areal densities. Two layers of Nanocomp sheet, for example, have approximately the same shielding effectiveness as the traditional metallic over-braid but at slightly more than one percent of the original weight. There is only a marginal increase in the shielding effectiveness of two layers versus one layer due to the fact that most of the shielding comes from the optical opacity of the tape which is not dependent linearly with thickness. One layer of the CCNI buckypaper performed slightly better than the Nanocomp sheets; buckypaper is not available at production quantities.

The caveat to these results is that the carbon nanotubes materials have a higher resistivity than metal – meaning that their low frequency shielding performance is not acceptable nor can they provide adequate lightning strike protection. A logical application of CNTs for shielding would be to replace one metallic layer in a dual braid construction, utilizing the metal for the low frequency and the carbon nanotubes for the high frequency.

2. Cable Prototype Builds

The first cable prototypes were coaxial constructions for comparison to standard RG-316 cables; insertion loss testing shows poor results. The attention (in dB/100 ft or db/30.48m) versus frequency (10Mz to 10 GHz) is shown in Figure 3. The red squares represent MIL-C-17/113C specification for the cable; the standard all copper construction follows the specification in the lowest (blue) line. The center (purple) line is a CNT shielded cable with copper conductor. The top line (green) is an all-CNT construction. The significant attenuation seen in the all-CNT construction can be attributed to its poor conductivity as well as irregularities in the CNT yarn geometry.

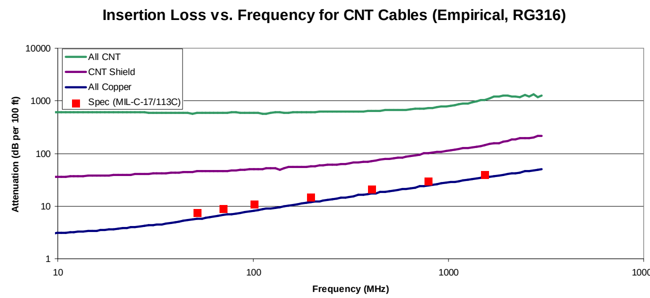
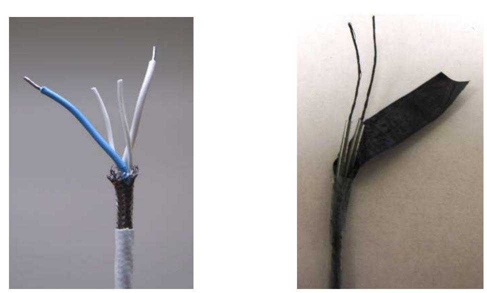


Figure 3. Insertion Loss (dB/100 ft or dB/30.48m) Testing for Various Constructions

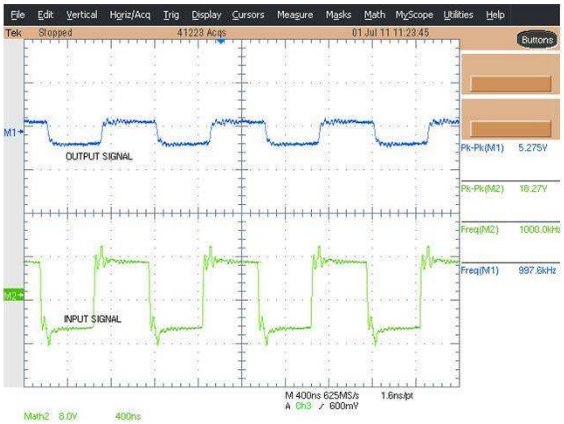
The second series of prototypes were all CNT twisted pair for comparison to standard copper cables used for MIL-STD 1553 applications. The all CNT cables were built using Nanocomp CNT yarn (26 AWG equivalent diameter) upon which an ETFE insulated layer was extruded by TE. The insulated yarn was then constructed into a twisted pair and a single layer of Nanocomp CNT tape was used as the shielding material as shown in Figure 4:



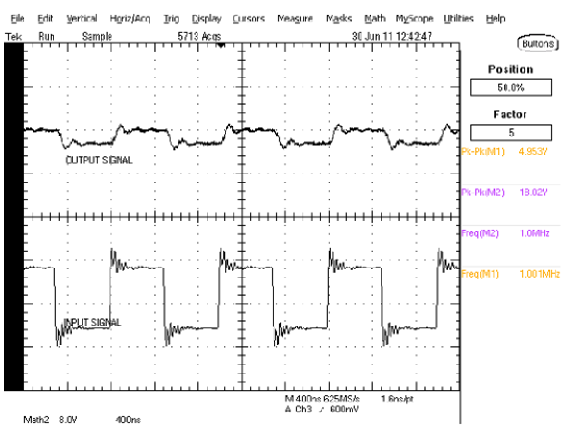
(a) (b)

Figure 4. Shielded twisted pairs. (a) standard copper construction (b) all CNT construction

The all CNT construction is 69% lighter than the standard cable. A comparison of between the two cables during a 1 MHz signal test of an approximately 3 meter cable showed a 12.995 V drop for the copper data bus and 13.067 V drop for the all CNT data bus (effectively, both had a 13V drop.) Screen captures are shown in Figure 5:



(a) Copper



(b) CNT

Figure 5. Signal data from (a) standard copper construction with 12.995 Volt drop (b) all CNT construction with 13.067 Volt drop.

A third cable, an IEEE-1394 prototype, was recently built using Applied Nanostructured Solutions CNS material. Electrical testing is still underway as of the time of this writing but the material can be processed successful in a standard commercial braiding system as seen in Figure 6:

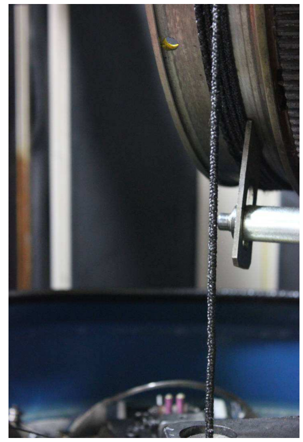


Figure 6. Carbon NanoStructures Braided onto an IEEE 1394 core

3. CNT Material Terminations

The high resistivity of macroscopic CNT structures allows the use of standard crimp technologies in terminating CNT cables and shields [5]. A comparison of phosphor bronze socket/brass pin F-crimps made on CNT yarn (24 AWG diameter equivalent) and copper strands, and the resulting densification, is shown in Figure 7:

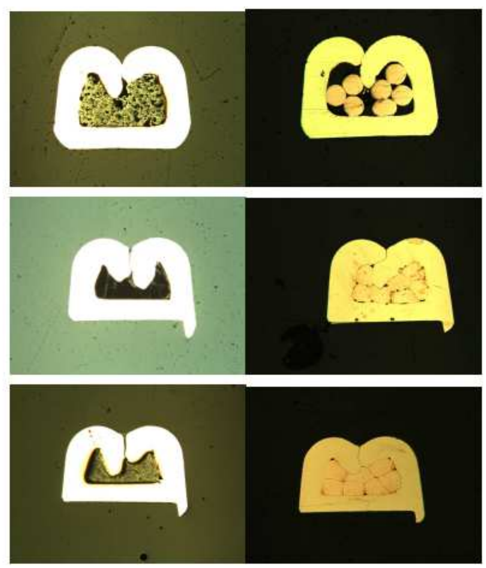


Figure 7. Cross section of CNT (left) versus Copper (right) F crimps; crimp height variation of large, standard, small, 37.5x magnification

Similar densification can be in seen in success cross sections of CNT yarn (24 AWG equivalent diameter) in a tin-plated O-crimp, as imaged with SEM, in Figure 8:

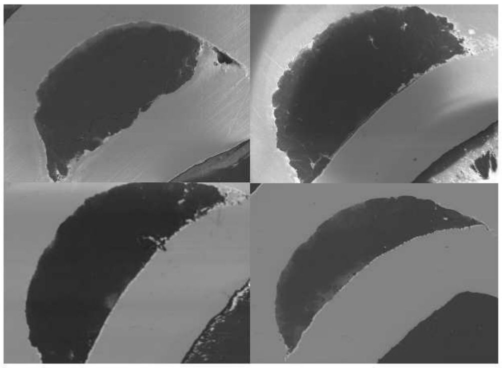


Figure 8. Successive cross-sections in increasing proximity to the tightest point of the crimp.

The O crimps were also tested for mechanical strength using an Instron load frame with the crimp termination clamped in the lower tensile jaw and the yarn wrapped around the upper capstan grip, as shown in Figure 9. The sample was approximately 55 cm long and the pull speed was 5mm/minute. Note that a snorkel was placed near the test set-up and a vacuum was pulled through a portable HEPA filter system to pick up any possible CNT debris at yarn failure.

Figure 9. Tensile Test Set-Up.

Three sets of samples were tested; none failed by pullout but from yarn breakage far from the grip. The average maximum load (mean) was 78.69 +/- 0.58N; this is consistent with the yarn breakage strength in the absence of any crimps, shown in figure 10:

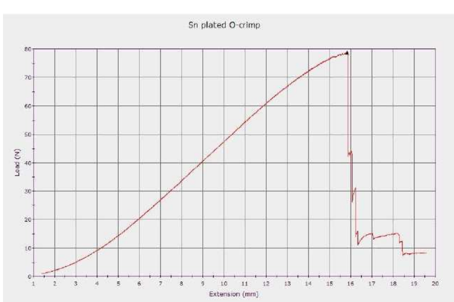


Figure 10. Typical Tensile Test Curve for Tin-Plated O-Crimp of CNT Yarn (24 AWG Diameter Equivalent)

The material manufacturer reports an ultimate breaking strength of 84 N, consistent with these results. Electrical contact resistance of the CNT yarn was slightly less than 0.2% of the resistance of the yarn, regardless of the crimp type (O or F) and the plating material used inside the crimp (nickel, tin, gold, brass.) We have also successfully soldered terminations to CNT yarns and tapes by first applying a metallic plated layer.

4. Limitations

Shielding effectiveness experiments and cable builds have highlighted the limitations of carbon nanotubes based materials – low frequency performance. While single walled carbon nanotubes electrical conductivity far exceeds that of copper [3], those novel properties observed in a single nanotube or graphene platelet quickly deteriorate when agglomerated into a macroscopic structure. The conductivity of commercially available yarns and tapes made from single- and dual-walled carbon nanotubes is orders of magnitude *lower* as shown in Figure 11:

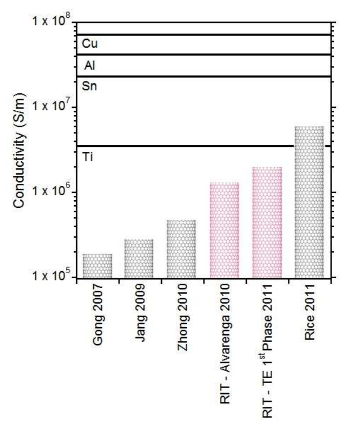


Figure 11. Conductivity of macroscopic CNT structures

[Private communication, Professor Brian Landi, RIT]

There are significant research efforts globally to grow, or modify, CNTs for high conductivity performance at macroscopic scales. The highest conductivity to date has been achieved with iodine doping at Rice University [4.]

5. Environmental Health and Safety

Inhalation hazard is the primary concern when using CNT materials; unbound CNTs are considered hazardous, based on testing in mice [6]. Long-term exposure effects to CNTs in macroscopic formats (e.g. non-woven tapes or spun yarns) have not yet been determined. It is believed that nanomaterials, including CNTs, encased in a solid matrix or under coating are bound and not considered hazardous.

Therefore, the greatest risk for exposure takes place in the manufacturing process of the tapes or yarns into finished articles. Material abrasion can take place as the CNT yarns and tapes move through traditional wire and cable manufacturing equipment. We have taken a conservative approach of setting up engineering controls to limit CNT exposure to the manufacturing team with industrial hygiene testing by an external group to track the level of particulates created in the braiding, twisting, extrusion, and assembly processes.

CNT fibers are handled using gloves and under a HEPA-filtered hood. If HEPA filtration is not available, a P-100 mask or double barreled respirator is used. Mechanical handling of CNT fibers is done in a contained environment with dedicated ventilation through HEPA filtration, as shown in Figure 12.

(a)

(b)

Figure 12: (a) Nan Yang Braider in a modular soft-walled cleanroom (b) HEPA filtration unit and ventilation system.

Independent monitoring of the braider set up above measured less than 7µg/m^3 of elemental carbon over an 8-hour time weighted average work shift. This limit is the lowest level that can be accurately measured using NIOSH 5050 but the level is considered an excess risk for lung effects [7]

6. Conclusions

As high volume quantities of CNT sheets, tapes, and yarns become available an opportunity exists in the wire and cable industry to leverage these low density materials for the development of products with dramatic weight savings over existing cables. We have examined several commercially available form factors as well as in-house fabricated substrates to understand the performance characteristics of CNTs tapes and yarns. Immediate applications include high frequency shielding and low to moderate rate data transmission cables. Attenuation losses in coaxial cables were high using CNT center conductor; high speed data transmission and power cable constructions are not yet possible with material available on the market.

To move beyond the prototype and niche product stage the following improvements must occur:

(a) Increased electrical conductivity of commercially available form factors.

(b) Robust insertion into existing manufacturing infrastructure to avoid retooling expenses, and

(c) A clear understanding of the environmental, safety, and health impact of these materials and a qualified set of engineering and administrative controls for risk-minimized manufacturing.

7. Acknowledgments

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8. References

[1] Baughman, Ray H., Zakhidov, Anvar A., de Heer, Walt A., "Carbon Nanotubes – the Route Toward Applications," Science, 297(5582), 787-792 (2002.)

[2] Jarosz, et al, "High Performance, Lightweight Coaxial Cable from Carbon Nanotube Conductors," ACS Appl. Mater. Interfaces, 4, 1103-1109 (2012.)

[3] Jorio, A., Dresselhaus M., and Dresselhaus, G, eds, Carbon Nanotubes: Advanced Topics in Synthesis, Structure, Properties and Applications, Springer (2008.)

[4] Zhao, et al, "Iodine Doped Carbon Nanotube Cables Exceding Specific Electrical Conductivity of Metals", Science Reports, 1, 83 (2011.)

[5] Hemond, et al, "Evaluation of Crimping as Termination Technique for Carbon Nanotube Macro-structures," 58th IEEE Hold conference on Electrical Contacts, in press.

[6] Lam, et al, "Pulmonary Toxicity of Single-Wall Carbon Nanotubes in Mice 7 and 90 Days after Intertracheal Instillation", Toxicological Sciences, 77, 126-134 (2004.)

[7] NIOSH Current Intelligence Bulletin, "Occupational Exposure to Carbon Nanotubes and Nanofibers" retrieved from **http://www.cdc.gov/niosh/docket/review/docket161a/pdfs/carbonNanotubeCIB_PublicReviewOfDraft.pdf**

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