

SYNTHETIC METALS: POTENTIAL FOR
INDUSTRIAL VEHICLE ELECTRICAL
APPLICATIONS

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Synthetic Metals: Potential for Industrial
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By

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ABSTRACT

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Synthetic metals are a branch of material science that deals with conducting organic molecules. The quantum mechanics of these materials show that doping can fundamentally change the conduction method and significantly increase their conductivity. Addition of conductive fillers to these synthetic metals can create a composite with even higher conductivities, with the most promising being carbon nanotubes. Ultimately, most of the research into synthetic metals is utilized for the creation of new technologies, but replacing metal in existing systems has many benefits, such as lighter weight and improved corrosion resistance. Industrial vehicle electrical systems are one such system that could benefit from synthetic metals via simplified manufacturing, assembly, and increased robustness. This paper explores the conduction methods in synthetic metals and carbon nanotubes, looks at past research on synthetic metals and conductive composites, and postulates what future research would be required to make synthetic metals commercially viable in existing industrial vehicle applications.

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1. INTRODUCTION

The argument can be made that metals have played the biggest role in the advancement of mankind from a materials standpoint. Metals have been highly utilized in nearly all aspects of our culture from architecture and engineering to art and religion. This can be attributed to their unique combination of properties. Metals are typically highly conductive, formable, strong, hard, and in certain cases, corrosion resistant. However, they are also dense, highly reactive to certain compounds, and can be expensive to process. The limitations of metals have brought about the branch of material science called Synthetic Metals, which focuses on synthetic replacements with the desirable properties of metals, but without aforementioned negatives.

The synthetic metal research of interest in this paper deals with conductive synthetic metals. These materials have the potential to replace metals in electrical applications, which could result in lighter and more durable electronics. One such application is in the electrical systems of vehicles. Passenger vehicles would benefit from the weight savings to improve fuel economy. Industrial vehicles would benefit from the inherent corrosion resistance that synthetic metals could provide.

A large amount of engineering resources and therefore cost of an industrial vehicle is devoted to corrosion protection. Not only are the exposed structural surfaces protected via paints, decals, and polymer coatings, but a significant amount of resources are devoted to seals for internal components. Electrical components, like connectors and the fuse relays, require water tight seals to protect the contacts from corrosion. This corrosion not only comes from water, but from other chemicals that might be in the industrial vehicle's envi-

ronment. In this regard, a synthetic metal that could replace traditional metal contacts in electrical connectors and fuse relay centers could reduce complexity, cost, and failures in the electrical systems of industrial vehicles.

This paper will focus on existing research in intrinsically conducting polymers, ways to increase the conductive properties of such polymers, and composites utilizing such polymers. The paper will conclude with a brief case study of a potential application for synthetic metals, and speculate on what research is still required before such materials can become commercially viable.

2. LITERATURE REVIEW

2.1 Inherently Conductive Polymers

Inherently conductive polymers were an accidental discovery. As the story goes, a Japanese graduate student was attempting to polymerize acetylene but instead of a material related to polyolefins, the graduate student created a material that had a silver, metallic appearance. The professor overseeing the research, Dr. Hideki Shirakawa, performed tests on the polymer and discovered the polymer was significantly more conductive than any polymer he had previously tested. The new material was brought to the University of Pennsylvania where research into synthetic metals was already underway. Dr. Shirakawa worked with Allen MacDiarmid and Alan Heeger to improve the conductivity of polyacetylene. The three discovered that much like other semiconductors, doping increased the conductivity of the material. Polyacetylene seemed to respond well to doping with iodine and the first report of their findings occurred in 1977 (Epstein, 1999). The researchers claimed they created an iodine doped polyacetylene with conductivity on the order of 10^7 Siemens/m (Strong, 2006), which is on the order of steel and greater than the tin and lead which comprises solder.

The primary conductive path in polyacetylene is the conjugated carbon bonds along the polymer chain's backbone. This is what the Japanese graduate student created. In its saturated form, polyacetylene is not any more conductive than polyethylene, but when unsaturated, the carbon bonds along the backbone form alternating single/double bonds to create a conjugated carbon backbone. Sigma bonding in carbon is very stable and the shared electrons are held tightly to the atom per Figure 1.

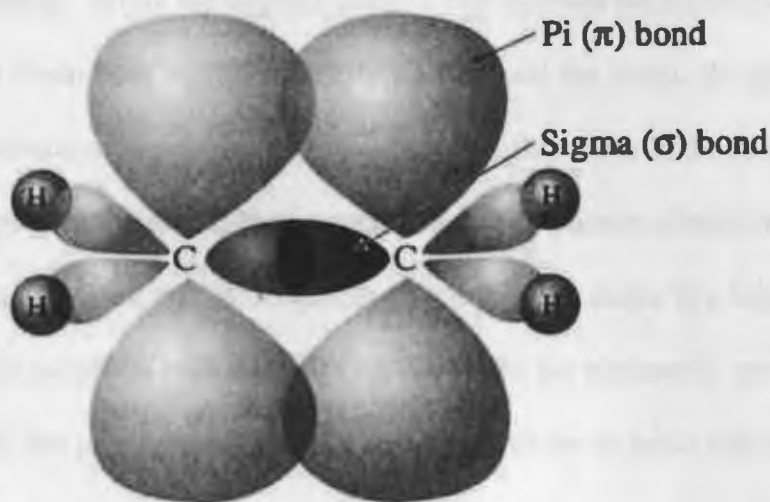


Figure 1: Sigma and Pi bonding in a carbon atom (Stejskal, 2002).

Pi bonds are further from the nucleus and the shared electrons are bound to the atom less tightly. In the case of conjugated carbon bonding, the alternating single and double bonds create a chain like structure shown in Figure 2. Introducing an electron into the beginning of the chain alters the sequence of the single and double bonds and ‘pops’ an electron out the end of the chain.

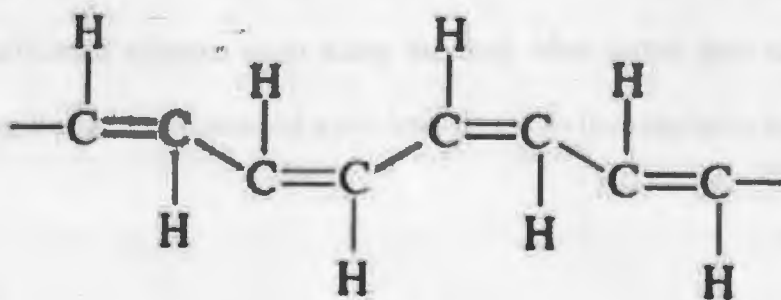


Figure 2: Conjugated carbon bonding in polyacetylene (Stejskal, 2002).

The dynamic alteration in the carbon bonding along the backbone chain is called a polaron. A polaron is a slow moving polarization field that typically accompanies a mov-

ing charged particle. While the original electron that initiates the polaron at the beginning of the polymer chain does not continuously move down the chain, the polaron it creates does. As the polaron moves down the chain it creates distortions in the nearby surrounding material. The polaron is assisted by the polymers natural phonon vibrations. A phonon, in quantum mechanics, is the natural frequency of a material's atoms in a lattice. As the carbon atoms in the polymers backbone vibrate, the bonds are alternately stretched and compressed. Due to the pi bonds weaker state, stretching of the pi bond will cause it to break and re-pair with the closer neighboring carbon atom and form the pi bond there. The phonon behavior of the polymer backbone assists in the switching of the pi bonds down the polymers backbone, transferring an electron, and keeping the polaron moving until the end of the polymer chain.

Not all conducting polymers are made up of conjugated carbon bonds along the backbone, but while some utilize additional atoms or aromatic rings along the backbone, there is still a conjugated carbon path. A few of these intrinsically conductive polymers can be seen in Figure 3. Polyaniline, which can be injection molded like traditional thermoplastics, utilizes a nitrogen atom along the back bone rather than conjugated carbon atoms. Polyaniline will be discussed again later due to its thermoplastic nature.

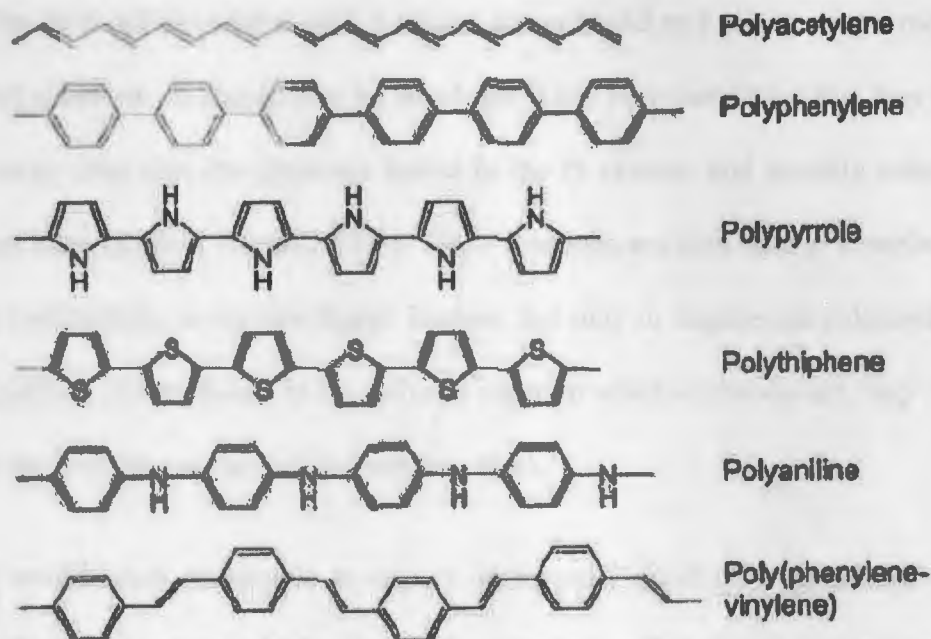


Figure 3: Intrinsically conducting polymers (Roth & Carroll, 2004).

2.2 Solitons and Doping in Conducting Polymers

Another key phenomenon in intrinsically conducting polymers are Solitons. Solitons are simply defined as “quasiparticles corresponding to solitary waves” (Roth & Carroll, 2004). These standing waves are created by naturally occurring or artificially induced defects in the polymer chain. In polyacetylene there naturally exists about 400 solitons per 10^6 carbon atoms (Roth & Carroll, 2004). Solitons are created by the breaking of a double bond along the back bone, which results in the splitting of an electron pair between carbon atoms. This creates a particle duality, a soliton and antisoliton, as shown in Figure 4.

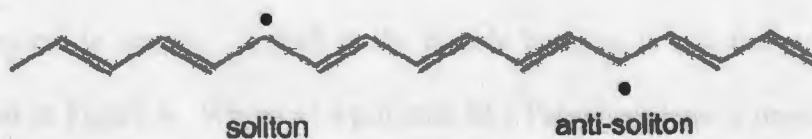


Figure 4: Soliton and Antisoliton in polyacetylene (Roth & Carroll, 2004).

The electrons associated with a soliton are unbound and able to move more freely than bound electrons. It should also be noted that it has been postulated that they exist in a higher energy state than the electrons bound in the Pi valence and actually belong to the conduction band (Roth & Carroll, 2004). These electrons are then able to contribute to the polymers conductivity as mobile charge carriers, but only in degenerate polymers. Otherwise the solitons create 'holes' in the polymer chain in which electrons can 'hop' from one soliton to the next, due to the unfilled electron shell.

It would seem reasonable to expect intrinsically conductive polymers with high numbers of solitons to have a higher level of conductivity. This was in fact proven with the first experiments completed on doped polyacetylene. Doping a conjugated polymer can create additional solitons on the polymer chain, which increases the polymers conductivity. This is represented in Figure 5. The dopant is typically an electron accepting atom which creates a positively charged soliton site and a negatively charged dopant after the bond has been made.

Iodine was first used to dope Polyacetylene back in the original experiments completed in 1977. The result was a conductivity increase many orders of magnitude larger than undoped polyacetylene (Roth & Carroll, 2004). Not all conductive polymers react the same way to doping. The effect of doping depends on if the polymer is degenerate or non-degenerate. Degenerate polymers do not care which sites the double bonds occupy, as both states are identical in energy. A shift in the double bonding is still the polymers ground state, as shown in Figure 6. Where as a polymer like Polyphenylene is transformed from a

ground state to a raised energy state through the aromatic rings. The rings change from aromatic, having three double bonds, to quinoidal, having two double bonds.

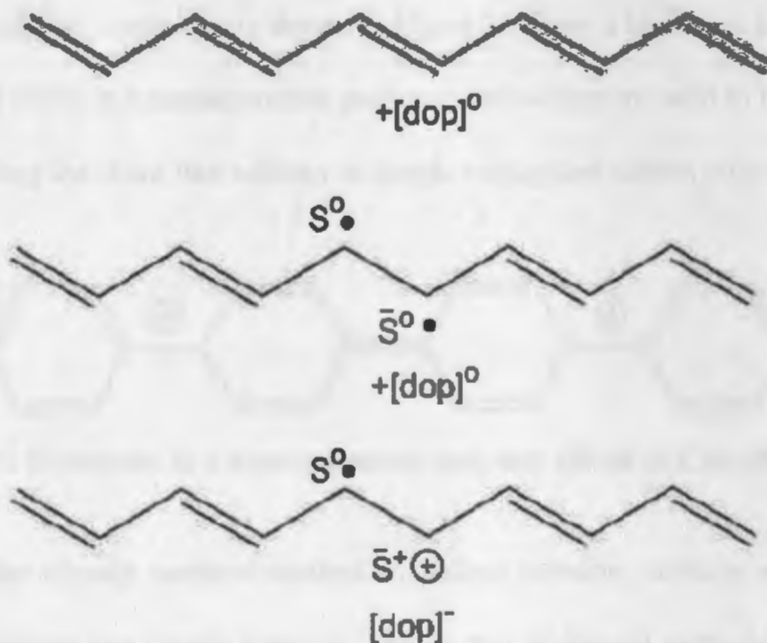


Figure 5: Soliton creation in polyacetylene through doping (Roth & Carroll, 2004).

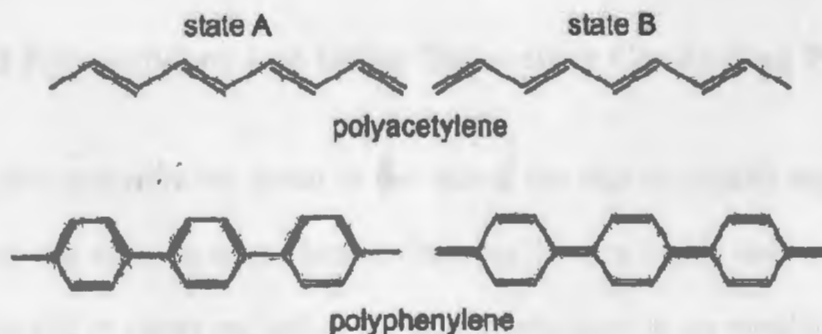


Figure 6: Degenerate versus nondegenerate polymer states (Roth & Carroll, 2004).

Soliton creation in polyacetylene results in a mobile soliton. Where the soliton resides does not change the energy state of the polymer chain, whereas soliton creation in nondegenerate polymers, like Polyphenylene, create a higher energy state along the rest of the polymer chain. Solitons are forced to the ends of the polymer chains to minimize the

energy state of the polymer and return the quinoidal rings to aromatic rings. For this reason stable solitons are created in pairs called Bipolarons in nondegenerate polymers (Roth & Carroll, 2004). These bipolarons are forced close together to minimize the high energy regions of the polymer chain, this is shown in Figure 7. Since a bipolaron is needed for the solitons to exist stably in a nondegenerate polymer, the solitons are said to be fixed and unable to move along the chain like solitons in simple conjugated carbon polymers.



Figure 7: Bipolaron in a nondegenerate polymer (Roth & Carroll, 2004).

Besides the already mention method of soliton creation, solitons also are created from photogeneration and charge injection. These two additional methods are outside the scope of this paper and will not be covered in detail.

2.3 Doped Polyacetylene and Other Degenerate Conducting Polymers

Conductive polymers are found in two states, the neat or slightly doped state is a semiconductor and depends upon electron 'hopping', where highly doped polymers are considered metallic in nature and utilize the large charge store in the metallic band to conduct rather than the phonon assisted quantum mechanical tunneling found in the semiconducting polymers (Roth & Carroll, 2004). Both states depend upon electrons freeing themselves from the Pi valence band and moving into the conduction band. Therefore there has been significant research into the temperature dependant conductivity of intrinsically conducting polymers. Figure 8 shows the conductivity of polyacetylene with doping levels

from light to heavy with respect to temperature. The conductivity is plotted along with the conductivity of some common metallic conductors.

One thing to be noted from Figure 8 is that as the temperature decreases, so does the conductivity of polyacetylene. Highly conductive metals tend toward superconducting nature with decreasing temperature, but the reduction in thermal energy reduces the mobility of the electrons associated with the solitons in the polymer. Interestingly, the more highly conductive metallic polyacetylene was less affected by temperature than the low doped semiconducting samples. Figure 9 shows the conductivity of a highly doped and reasonably doped polyacetylene versus temperature in better detail.

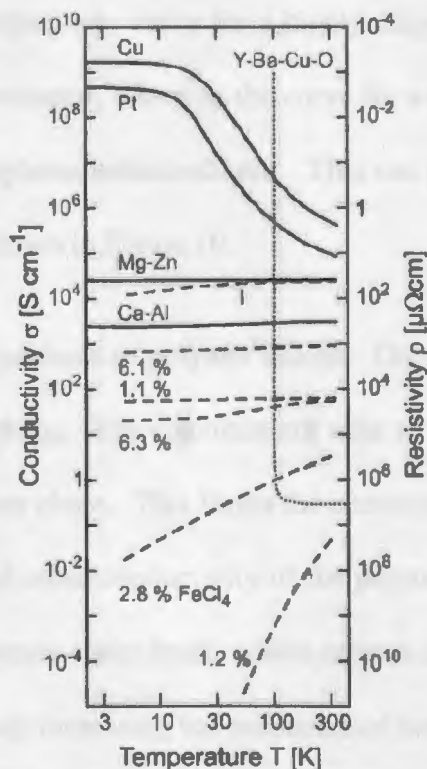


Figure 8: Conductivity of polyacetylene and metallic conductors versus temperature (Roth & Carroll, 2004).

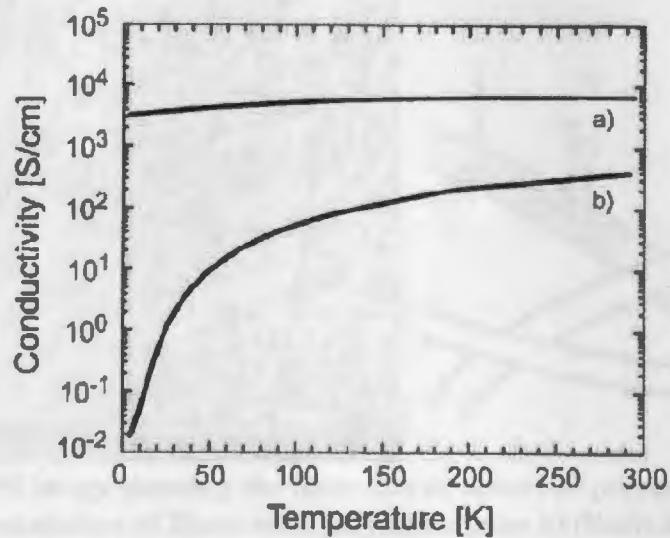


Figure 9: Conductivity of a highly doped a) and moderately doped b) polyacetylene versus temperature (Roth & Carroll, 2004).

One can note the conductivity curve for a highly doped polyacetylene follows that of an amorphous metallic conductor, whereas the curve for a moderately doped polyacetylene follows that of an amorphous semiconductor. This can partially be explained by the structure of polyacetylene, shown in Figure 10.

Each fiber contains hundreds of polymer chains. The chains are only able to cross-conduct through soliton hopping. The electrons are able to hop from the soliton on one chain to the soliton on another chain. This limits the conductivity of polyacetylene due to the porous nature and limited cross-conductivity of the polymer chains. The best conductive paths are along the polymer chain itself, which creates electron backscattering in the material as a whole, effectively increasing the resistance of the material.

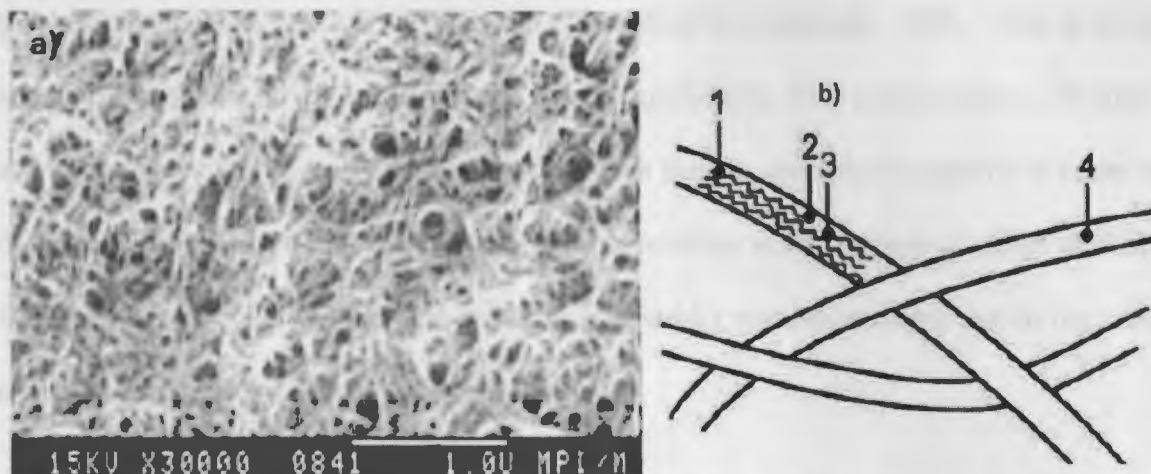


Figure 10: SEM image showing the fiber-like structure of polyacetylene a), and graphical representation of fibers with polymer chains b) (Roth & Carroll, 2004).

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This leads to another method to increase the conductivity of polymers, polymer chain alignment. The easiest method of aligning the polymer chains is by stretching the material. Stretch alignment experiments on polyacetylene have shown to increase the conductivity 25 times (Roth & Carroll, 2004). However, the material becomes highly anisotropic.

Experiments with polythiophene have had similar results. Stretched polythiophene-*nevinylene* has been found to have conductivities as high as 2000 S/cm where as the un-

stressed material has conductivity of 80 S/cm (Schopf & Kobmehl, 1997). This is an increase of 25 times, which matches well to the experiments with polyacetylene. Furthermore, experiments with polythiophene have shown that an amorphous material is easier to dope and improve the conductivity over semicrystalline polythiophene (Schopf & Kobmehl, 1997). However, crystalline material is generally more conductive due to the close packing of the chains allowing soliton hopping.

Unfortunately, polyacetylene is unstable in oxygen environments. The material undergoes irreversible oxidation to form carboxyl groups along the backbone of the polymer chain (Pron & Rannou, 2002). The carboxyl group breaks the pattern of conjugated bonds in the backbone, effectively rendering the polymer chain nonconductive.

2.4 Doped Polyaniline and Other Nondegenerate Conducting Polymers

Polyaniline (PANI) is a nondegenerate conducting polymer, as was mentioned in the previous section. Doping of polyaniline and other nondegenerate polymers is fundamentally different than degenerate polymers due to the unstable nature of the solitons produced on the polymer backbone. Solitons produced singly are forced to the ends of the chain to minimize the number of quinoidal rings in the polymer chain. This leads to bipolaron formation to create static, stable solitons on the backbone. One advantage of polyaniline is that in its doped form it is very stable in an oxygen environment, showing little change in conductivity over long periods (Pron & Rannou, 2002).

There are multiple ways to dope polyaniline. Protonic acid doping and oxidative doping can produce the emeraldine salt form of polyaniline, which is depicted in Figure 11

(Epstein, 1999). Emeraldine base form of PANI is difficult to dissolve into a solvent. This is due to amine groups acting as hydrogen donors and imine groups of adjacent chains acting as hydrogen acceptors, creating intermolecular hydrogen bonding (Pron & Rannou, 2002). This can be overcome by using mixed solvents that act as both hydrogen donors and hydrogen acceptors, creating a low viscosity polymer solvent capable of being spun into fibers or processed into films.

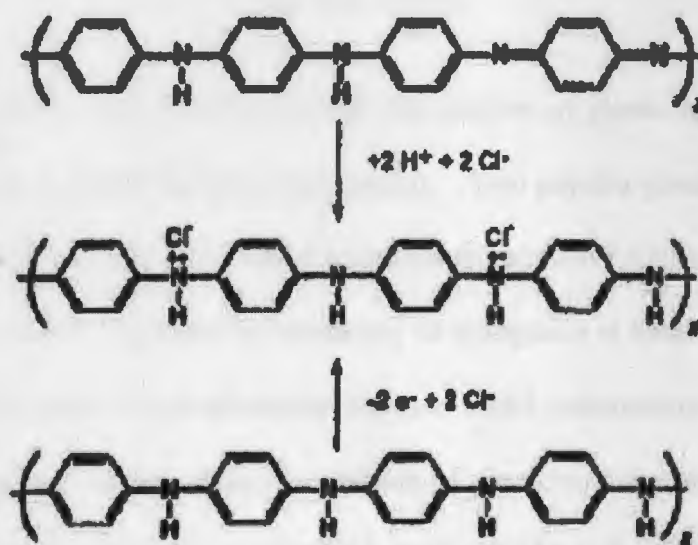


Figure 11: Formation of emeraldine salt form of polyaniline from protonic acid (top) and oxidative doping (bottom) (Epstein, 1999).

Another common way to dope polyaniline is through sulfonation. Figure 12 depicts sulfonated polyaniline. It is interesting to note that the 100% sulfonated polyaniline contains one quinoidal carbon ring per monomer. The quinoidal rings have been shown to interact with carbon nanotubes to transfer charge between the nanotubes and the polymer matrix (Mau & Dai, 2001).

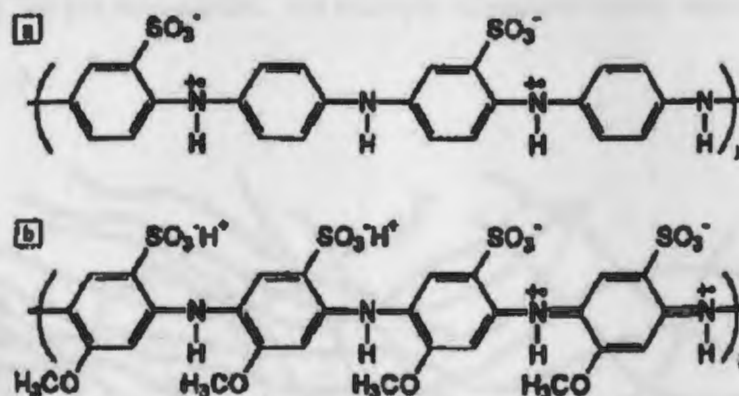


Figure 12: 50% Sulfonated (a) and 100% sulfonated (b) polyaniline monomers (Epstein, 1999).

A novel way to dope PANI is through the addition of plasticizers, which both increase the polymers conductivity and processability. Two popular plasticizers are diesters of phthalic acid and ethylhexyl ester, which when combined with PANI increase its conductivity and its mechanical properties by increasing its elongation at break to 45%. Where as dialkyl or dialkoxy ester of sulfophthalic increase PANI conductivity into the metallic range (Pron & Rannou, 2002). Also, the addition of plasticizers that do not add to PANI doping can increase the temperature range of metallic conductivity, like dioctyl phthalate, triphenylphosphate, or tritolyl phosphate (Pron & Rannou, 2002).

Crystallinity level plays a large role in the conductivity of conductive polymers. In highly doped samples, the crystalline regions allow the electrons to hop from chain to chain and conduct in a nearly metallic method. The charge is carried without regard to chain orientation in the ordered crystalline regions. The limiting factor for conductivity then lies in the amorphous regions. The density in these regions is often low and the electrons are only able to hop chains when the chains become close and if there is a soliton present. The transport method in these regions is then the soliton hopping method and phonon assisted

conduction along the polymer chains. An example of ordered versus amorphous regions is shown in Figure 13.

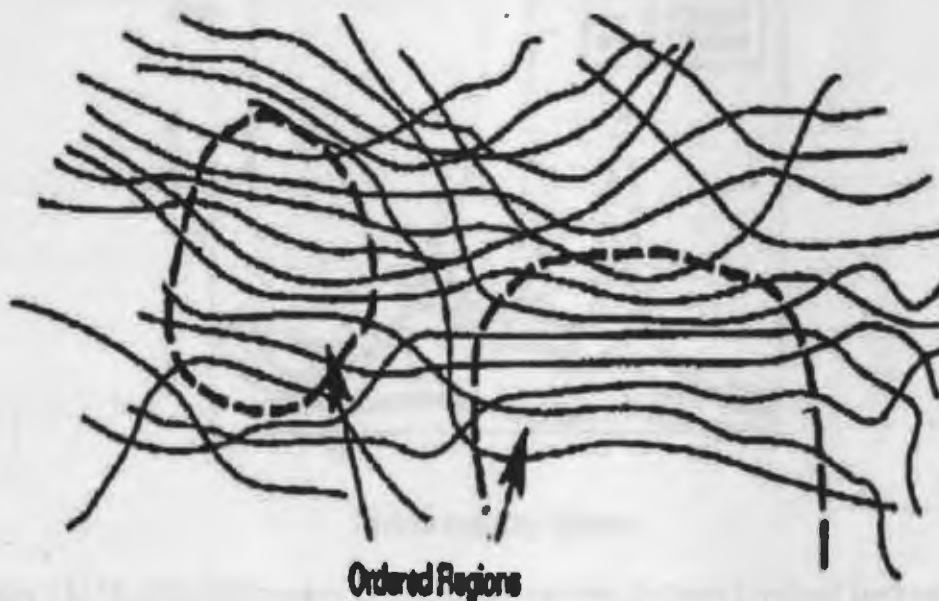


Figure 13: Ordered regions versus amorphous regions in a polymer (Epstein, 1999).

One method for doping polyaniline that has shown promise not only as a dopant, but also as a method of increasing crystallinity is camphor-sulphonic acid (Abell et al., 1999). Experiments with this dopant have shown that the high levels of crystallinity and metallic conductivity can be achieved with doping levels above 50%. X-ray diffraction was used to determine the level of crystallinity versus doping level, which can be seen in Figure 14. Conductivity was tested versus temperature for multiple doping levels, Figure 15. It is interesting to note that at 60% doping the combination of high crystallinity and high doping results in a metal like conductivity curve. Conductivity increases with decreasing temperature to about 100 K (-280 F), where it begins to decrease.

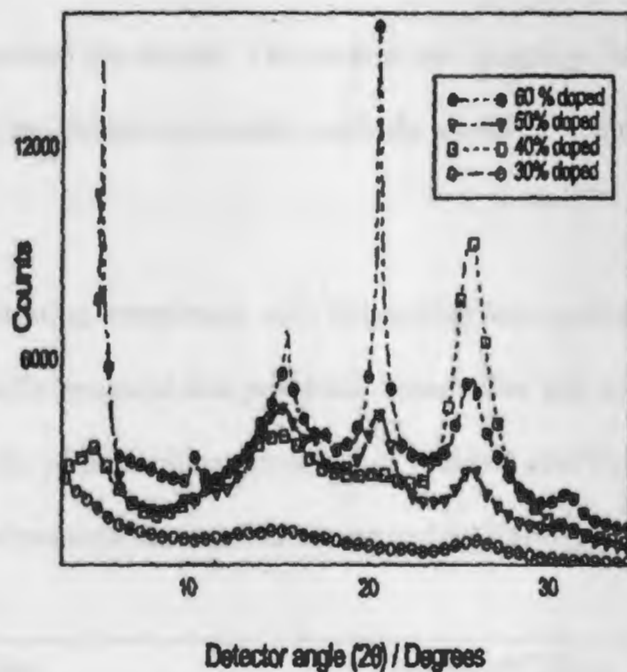


Figure 14: WAXS diffraction patterns for various doping levels of polyaniline (Abell et al., 1999).

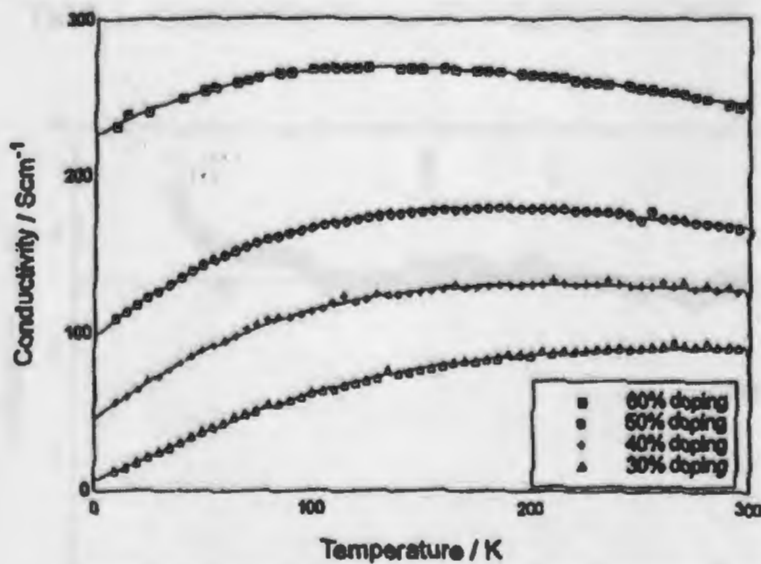


Figure 15: Conductivity of multiple doping levels of polyaniline versus temperature (Abell et al., 1999).

The main problem with this research is that all the samples were solvent cast, and the solvent also contained the dopant. This method isn't practical for mass production and additional research into thermo-processing methods would be required for mass production.

Another interesting experiment with Polyaniline was performed to determine the characteristics of easily produced and processed forms. One test was performed to determine the conductivity of polyaniline versus time. Table 1 and Figure 16 show data for doped polyaniline versus time for standard doping and PANI prepared with excess dopant.

Storage time	Conductivity ^a (S cm ⁻¹)	
	Standard PANI	PANI prepared in excess 1 M HCl
3 days	3.20 ± 0.04	9.94 ± 0.27
4 months	2.59 ± 0.06	12.70 ± 0.34
16 months	1.53 ± 0.03	6.91 ± 0.14
19 months	1.63 ± 0.02	6.87 ± 0.41

Table 1: Conductivity for aged PANI (Stejskal, 2002).

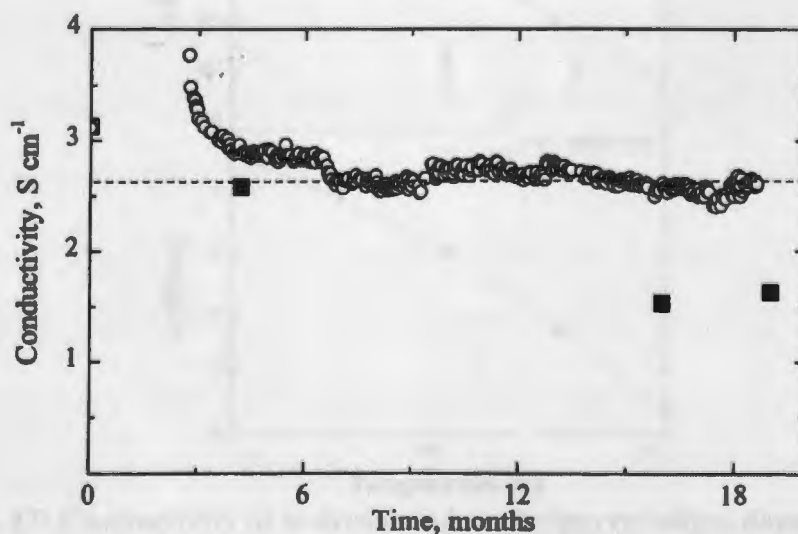


Figure 16: Conductivity for PANI versus age (Stejskal, 2002).

Table 1 shows the effect of utilizing extra dopant; an increase in conductivity with age at four months. Long term, PANI has a 50% reduction in conductivity for standard doped samples and about a 30% reduction in conductivity for excessively doped samples (Stejskal, 2002). In both cases, conductivity seems to stabilize around 8 months as shown in Figure 16.

Research by Varma and Xavier (2010) investigated the temperature stability of highly conductive polyaniline. Figure 17 shows polyaniline doped with Methylpyrrolidone (NMP) and polyaniline doped with m-cresol. The m-cresol dopant created a polyaniline with high conductivity, especially throughout the usable thermal range for typical wire harnesses. The plots of conductivity versus temperature in Figure 17 goes from -100F to 300F.

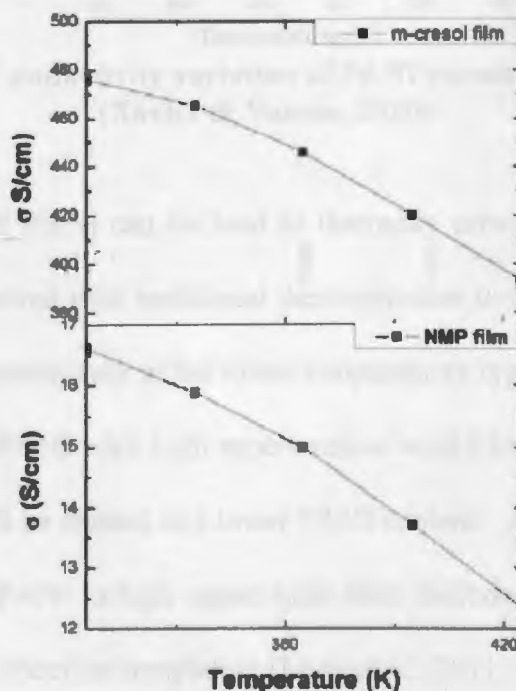


Figure 17: Conductivity of m-cresol and methylpyrrolidone doped PANI (Xavier & Varma, 2010).

Figure 18 shows the percent change of conductivity versus temperature for the doped PANI. Not only is the m-cresol doped PANI able to produce a material with higher conductivity, its variation with temperature is significantly lower than the NMP doped PANI over the temperature range shown. A conductivity of 47,300 S/m was found for the m-cresol doped PANI at the lower temperature (Xavier & Varma, 2010).

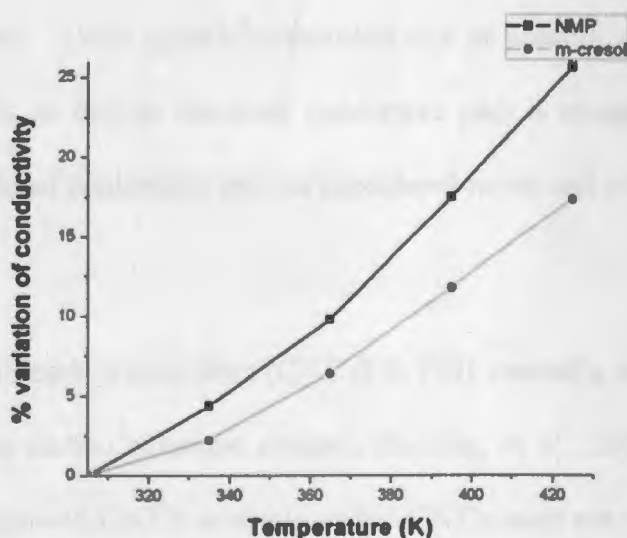


Figure 18: Conductivity variation of PANI versus temperature (Xavier & Varma, 2010).

Since highly doped PANI can be hard to thermally process, and contains superior conductivity, it can be mixed with traditional thermoplastics to create a composite. Since the PANI would not thermally mix at the lower temperatures typically used to process traditional resins, creating PANI with high aspect ratios would be ideal. The creation of a conductive network could be created at a lower PANI content. A number of methods used to create highly doped PANI in high aspect ratio form include hard physical templating, electrospinning, and soft chemical templating (Long et al., 2011).

2.5 Carbon Nanotubes

Conductive fillers have been used in traditional polymers for a number of years to create electromagnetic shields for electronic components. While this creates a cost effective EM shield, the conductivity of these fillers is typically very low. Carbon Black, graphite whiskers, and thin metallic wires have all been used to turn traditional polymers into conductive composites. These types of composites rely on creating a percolating network of filler in the matrix so that an electrical conductive path is created through the filler. These types of traditional composites are not considered novel and will not be explored in detail in this paper.

The discovery of carbon nanotubes (CNT's) in 1991 created a new sub-branch of nano-science devoted to carbon nanotube research (Schinar, et al., 2000). The early work was completed on multiwall CNT's as single walled CNT's were not discovered until 1993 and efficient synthesis of SWCNT's was not available until 1996 (Schinar et al., 2000). CNT's and especially SWCNT's were found to have excellent electrical properties. These properties are dependent upon the geometry and layout of the carbon atoms in the CNT.

Figure 19 shows the three arrangements possible for a SWCNT. Each CNT is typically capped by a half a fullerene molecule on each end, and this arrangement is the primary predictor of the relative diameter of the CNT (Dresselhaus et al., 2006; Schinar et al., 2000). CNT's that can be capped by a C_{60} fullerene have the smallest possible diameters and are called 'armchair' carbon nanotubes. The fullerene caps follow the 'isolated pentagon rule', which means that in some configurations a pentagon ring of carbon atoms is used to create a closed geometric shape, but that no two pentagons can exist side by

side(Dresselhaus et al., 2006; Schinar et al., 2000). It is for this reason that the next smallest possible diameter CNT is the 'zigzag' carbon nanotube arrangement. Arrangements in-between armchair and zigzag arrangements are simply considered chiral carbon nanotubes.

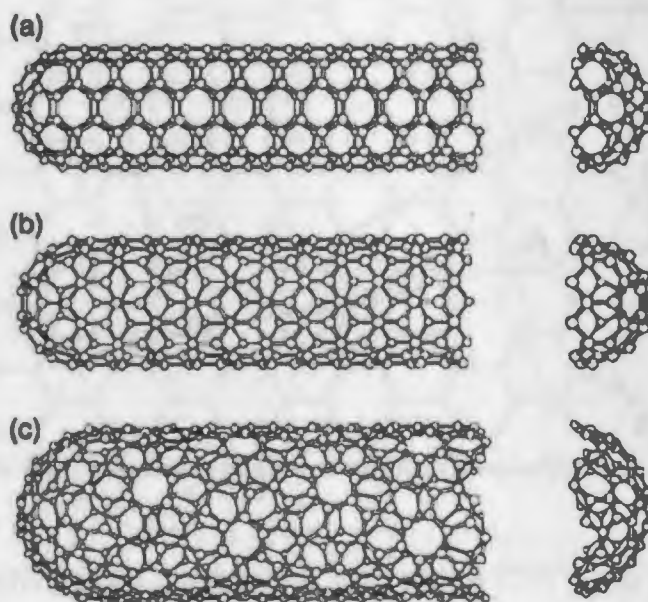


Figure 19: Armchair CNT (a), Zigzag CNT (b), and Chiral CNT (c) (Dresselhaus et al., 2006).

The chirality of CNT's is dependent upon the angle with which the carbon rings are assembled. An easy way to picture this is to think of a single sheet of graphene being rolled into a tube. The angle at which it is rolled is the chirality of the CNT. This is demonstrated in Figure 20.

The chiral vector C_h is defined by the unit vectors a_1 and a_2 (Dresselhaus et al., 2006; Schinar et al., 2000), which leads to designations of integers relating to the unit vectors of the form $(4,2)$, which is for vector C_h in Figure 20. Another common way to desig-

nate CNT's is by its diameter d and chiral angle Θ . This leads to designations for Armchair CNT's that are $(d, 30)$, zigzag are $(d, 0)$, and chiral CNT's have angles between 0 and 30.

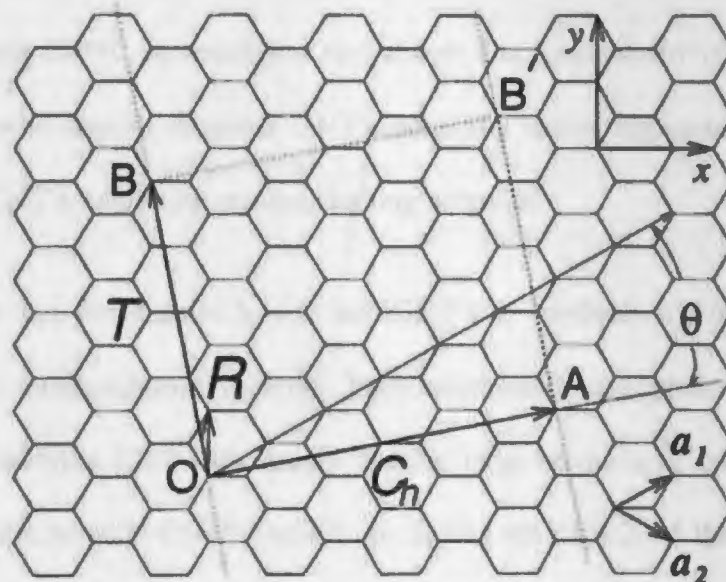


Figure 20: Chirality in carbon nanotubes (Dresselhaus et al., 2006).

Research performed on graphite was extended to CNT's and was found to model the conductivity of CNT's well. Specifically the calculations relating to electron mobility in a single sheet of graphene proved useful. A quantum mechanical equation relating the chirality of the CNT to the possible wave vectors for an electron located within the CNT was developed to predict if the CNT would have metallic or semiconducting behavior (Mintmire & White, 1994) (Endo, Lijima, & Dresselhaus, 1996). Verified by experimental results, it was determined that all Armchair CNT's are metallic, where as one third of all zigzag CNT's are metallic, and one third of all chiral CNT's are metallic. A simple equation to predict metallic behavior is shown in equation (1) (Epstein 1999).

$$n-m=3q \tag{1}$$

Where n and m are the integers of the unit vectors of the CNT and q is an integer. For example, an armchair CNT with unit vector (5,5) would be metallic, as would a zigzag CNT with unit vector (9,0), however, a zigzag CNT with unit vector (10,0) would be semiconducting (Harris, 2009). Research has also shown that conductivity is highly dependent upon diameter, with smaller diameter CNT's generally exhibiting metallic behavior and larger diameter CNT's exhibiting semiconducting behavior.

The issue then becomes of how to sort CNT's by conductivity, which is beneficial for transistor and semiconductor research. Early attempts at separation resulted in the destruction of the metallic CNT's by simply passing large amounts of current through the CNT mass until the metallic CNT's burned up. It was not until 2003 that a research team under Ralph Krupke hypothesized a way to selectively sort metallic CNT's from semiconducting (Harris, 2009). The team hypothesized that the dielectric constant for semiconducting CNT's is around 5, where as the dielectric constant for metallic CNT's is on the order of 1000. The dielectric constant for water is around 80, so suspending the CNT's in an aqueous solution and exposing them to an inhomogeneous electric field resulted in the metallic CNT's being drawn toward the electrode (Harris, 2009). This method was labor intensive as it included sonification to untangle the CNT's and centrifugation to purify the CNT solution from carbon soot and fullerenes. More work would need to be completed to make this method commercially viable.

A second method developed by the University of Connecticut utilized octadecylamine non-covalent functionalization to separate metallic and non-metallic CNT's (Harris, 2009). The theory was that metallic CNT's would be less susceptible to a reaction with the

solution. The semiconducting CNT's, on the other hand, would be dissolved leaving the metallic CNT's. This research was met with skepticism per Harris (2009).

Separation of CNT's can also be completed via gradient density ultracentrifugation. A selective surfactant can be applied to the CNT's that bond to certain chiralities, giving the metallic CNT's a different buoyancy. This method is able to produce CNT separation in the metallic layer of 70% metallic CNT's and 30% semiconducting (Arnold et al., 2006). Although not perfect, ultracentrifugation is able to produce appreciable quantities of metallic CNT's, even though the metallic layer of the centrifuged mass contains a significant number of semiconducting CNT's. Even though only 70% conducting CNT's are available, a percolating network of metallic CNT's in a polymer matrix should still be possible via this method of separation. An example of CNT separation using ultracentrifugation is shown in Figure 21. Due to their size and separation, the CNT layers absorb different wavelengths of light allowing for differentiation of the layers.

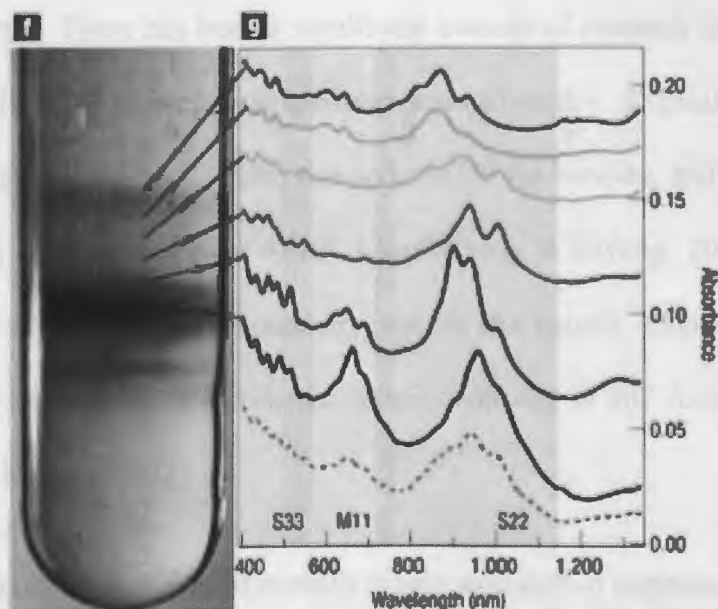


Figure 21: Separation of CNT's by ultracentrifugation (Arnold et al., 2006).

Figure 22 shows the wavelength absorption bands for the semiconducting CNT's as purple and yellow bands. The metallic absorption band is green and contains 70% conducting CNT's (Arnold et al., 2006).

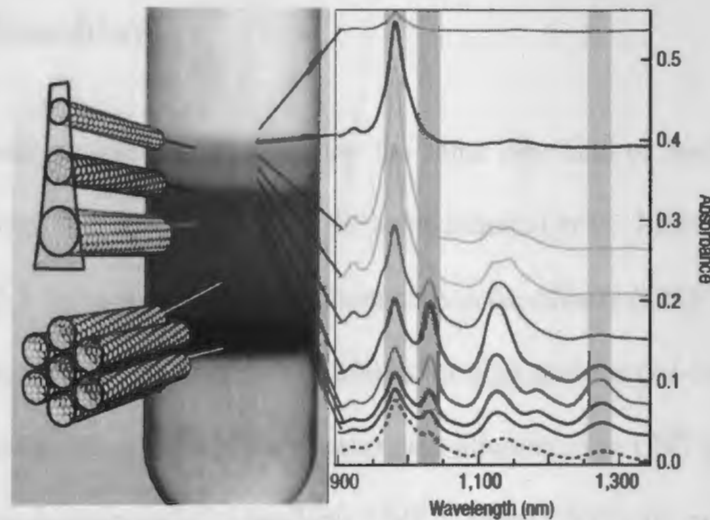


Figure 22: CNT identification via absorbance characteristics (Arnold et al., 2006).

Metallic CNT's have a very high conductivity, as their name implies, whereas semiconducting have been found to have resistivity on the order of 9.5×10^{-5} (Issi et al., 1995) (Endo et al., 1996). There has been a significant amount of research devoted to the conductivity of metallic CNT's, both as single tubes and as bundles. Typical conductivities for single tubes range from 10^5 to 10^6 S/m, and up to 3×10^6 for bundles, and in theory have the ability to carry a current density of 4×10^6 A/cm² (Hong & Myung, 2007). This current density is 10,000 times higher than conductive metals like copper. Copper has an electrical conductivity of 5.85×10^7 S/m and a current density capacity of 402 A/cm² in its high purity state (Hong & Myung, 2007).

Given the high conductivity of metallic single wall carbon nanotubes (M-SWCNT's), they are highly desirable for use in conductive composites. However, processing CNT's

can be challenging and a randomly oriented network of CNT's creates backscattering of electrons similar to the microstructure of polyacetylene discussed earlier. This backscattering creates limitations on the conductivity of the composite.

2.6 Carbon Nanofibers

While carbon nanofibers don't possess the same electrical or mechanical properties as carbon nanotubes, they also don't have the same inherent cost. Multi-wall carbon nanotubes tend to be 2-3 times more expensive than carbon nanofibers (CNF's), and single wall carbon nanotubes can reach as high as \$30,000/lb for high purities (Al-Saleh & Sundararaj, 2009). This makes commercial CNF's a lower cost alternative to CNT's. Pyrograf III nanofibers are one such commercially available CNF. These CNF's are produced by catalytic chemical vapor deposition, and typically utilize a hydrocarbon, like natural gas, propane, acetylene, or ethylene (Al-Saleh & Sundararaj, 2009). CNF's produced by this method have a typical conductivity of 250 S/cm, but this conductivity can be increased via post processing.

Much like CNT's, CNF's can have different morphologies based on the materials used to create them. Different catalysts and feed stocks produce different CNF's. For example, CNF's produced with propane tend to be linear, where as those produced with ethylene end up twisted, and those produced with acetylene typically have twisted, helical morphologies. Propane feed stock and nickel-copper catalyst produced the longest straightest CNF's with the highest surface area, but ethylene produces CNF's with the highest conductivity (Al-Saleh & Sundararaj, 2009). Table 2 outlines the differences between CNF's, CNT's, and traditional carbon fibers.

Property	VGCNF ^a	SWNT ^b	MWNT ^b	CF ^c
Diameter (nm)	50-200	0.6-1.8	5-50	7300
Length (μm)	50-100			3200
Aspect ratio	250-2000	100-10,000	100-10000	440
Density (g/cm ³)	2	~1.3 ^d	~1.75 ^e	1.74
Thermal conductivity (W/m K)	1950	3000-6000 ^f	3000-6000 ^f	20
Electrical resistivity (Ω cm)	1×10^{-4}	1×10^{-3} - 1×10^{-4}	2×10^{-3} - 1×10^{-4}	1.7×10^{-3}
Tensile strength (GPa)	2.92	50-500 ^g	10-60 ^g	3.8
Tensile modulus (GPa)	240	1500	1000	227

Table 2: Typical properties of CNF's, CNT's, and CF's (Al-Saleh & Sundararaj, 2009).

Much like CNT's, CNF's have a hollow core structure. They can be single layer or double layer, as shown in Figure 23. Figure 24 depicts the cup stacking of the graphene layers. The graphite planes are typically stacked in a nested manner resembling cups, hence the name. The inner and outer diameters of a single layer CNF are typically 25nm and 60nm, and a double layer CNF is typically 20nm and 83nm (Al-Saleh & Sundararaj, 2009).

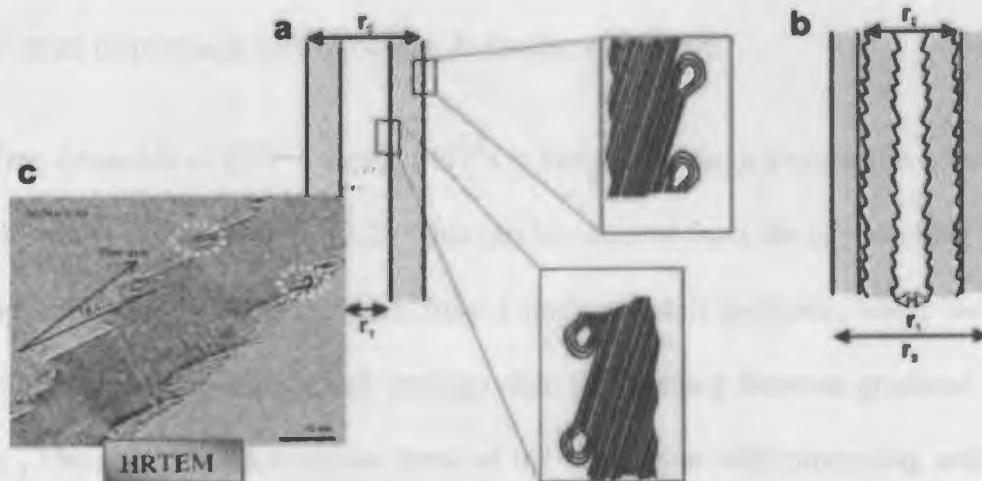


Figure 23: TEM image of single wall CNF and double wall CNF (Al-Saleh & Sundararaj, 2009).

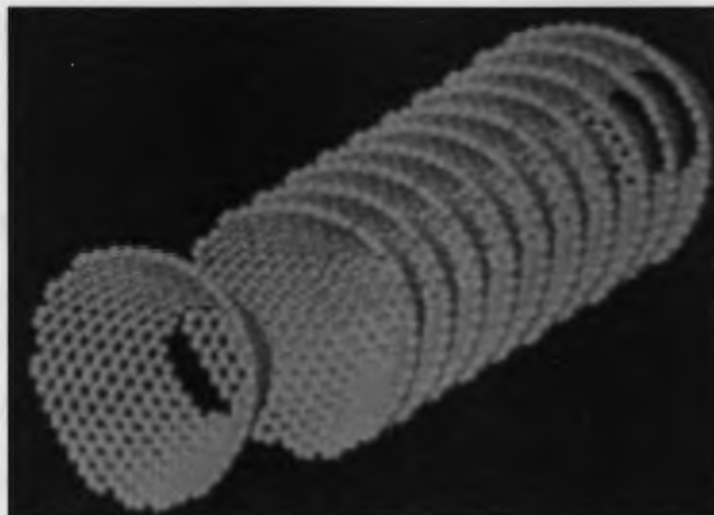


Figure 24: Cup stacking nature of CNF structure (Yong, 2007).

Carbon nanofibers are covered in amorphous carbon in their as produced state. This amorphous carbon decreases the conductivity of the fiber by providing a less conductive layer of carbon on the surface of the fiber. A number of methods are available to remove the amorphous graphite, but the method that both removes the amorphous graphite and increases crystallinity is graphitization. Graphitization includes heating the CNF's to 2800°C in an inert atmosphere (Al-Saleh & Sundararaj, 2009).

One downside to CNF's versus CNT's is that CNF's have a much lower mechanical strength, which is shown in Table 2. This can be inferred from the cup stacking nature of the graphene layers. CNT's are made from a single sheet of graphene, where the bonding between the carbon atoms is much stronger than the bonding between graphene layers in CNF's. The next section explores some of the challenges with processing and creating conductive composites and looks at some of the recent advancements to overcome these challenges.

2.7 Conductive Composites

Before the discovery of intrinsically conductive polymers, conductive fillers were added to traditional polymers to create conductive composites. These composites are not highly conductive so will only be briefly reviewed here.

Conductive fillers that were added to traditional thermoplastics and thermosets included high levels of carbon powder, carbon whiskers and fibers, powdered metals, metal wires, and other conductive fillers. Figure 25 shows various thermoplastics with weight percent of carbon black fill versus resistivity. While the drop in resistivity might be acceptable for creating a housing for electronics for protection from static build up and electromagnetic interference, the conductivity of these types of polymers will never reach the point of being a metal replacement.

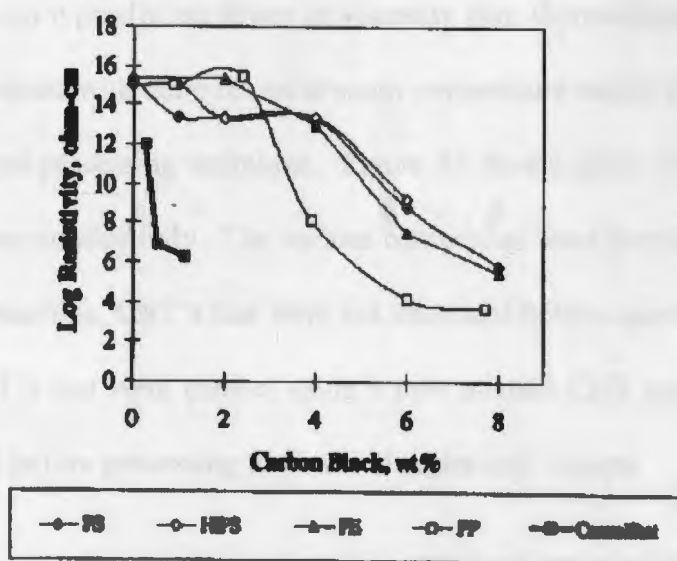


Figure 25: Thermoplastics with carbon black wt % versus resistivity (Moshe, 1999) (Rupprecht, 1999).

When CNT's were initially discovered to have high levels of electrical conductivity, these were also added to traditional polymers in an attempt to create conductive composites. However, there were mixed results. Researchers found that CNT's were inherently difficult to process due to their high aspect ratios and nano-size scale. MWCNT's processed better than SWCNT, because in early manufacturing of CNT's, MWCNT's tended to have straighter more aligned tubes. However, MWCNT's do not tend to be as conductive as SWCNT's, and their conductivity is highly dependent on the outer layers chirality. CNT's also tend to form clumps and become entangled with each other. These clumps of entangled CNT's can be difficult to separate, which is important to the conductivity of the composite.

Early attempts to create highly conductive composites used MWCNT's due to their easier processing and epoxies due to the lower viscosity of their unprocessed state. Epoxies are thermosets, so typically are lower in viscosity than thermoplastics in their uncured state, and can be mixed with nano-fillers at room temperature rather than requiring a high shear mixing thermo processing technique. Figure 26 shows epoxy MWCNT composites by fill percent versus conductivity. The various composites were prepared using traditional carbon black as a baseline, CNT's that were not sonicated before hand so contained entanglements, and CNT's that were created using a new aligned CNT manufacturing process and were sonicated before processing to remove tangles and clumps.

The aligned CNT's provided the highest increase in conductivity at the lowest fill percent. The entangled CNT's needed at least a 3% fill to create a conducting network, where the aligned CNT's only needed .5% fill. Compared to traditional carbon black, both

CNT arrangements required much less fill to create a conductive composite. Traditional carbon black required 15% fill by weight to reduce resistivity to a point to be useful as a static dissipating composite. Percolation thresholds as low as .1% wt CNT's have been reported though, which could make them more cost effective in the future (Spitalsky et al., 2010).

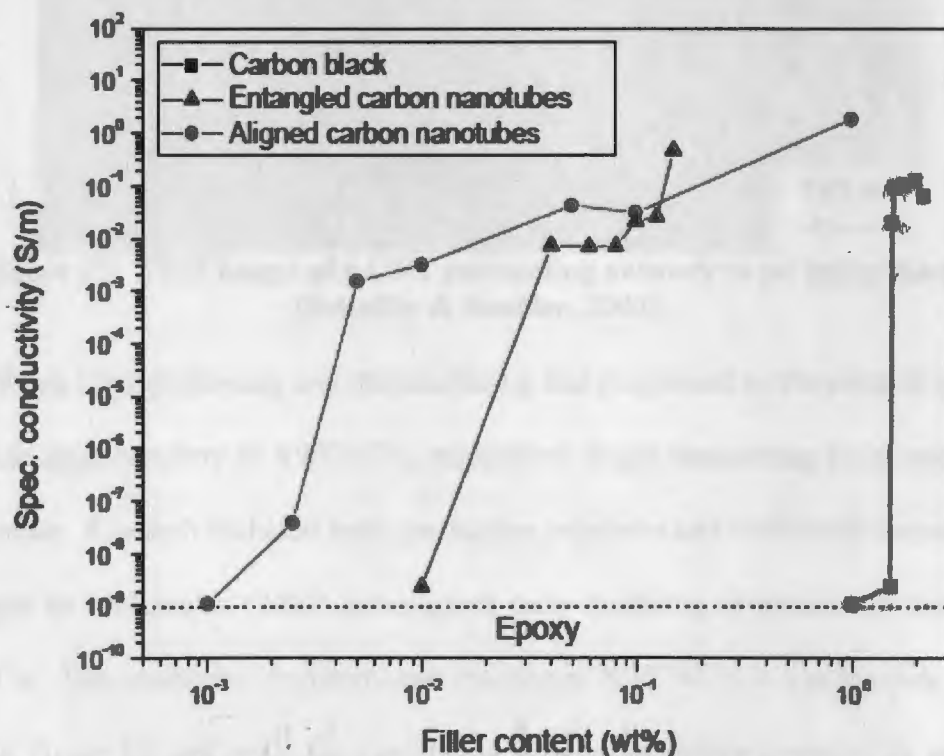


Figure 26: Epoxy MWCNT composites by weight percent of CNT fill and conductivity (Schaffer & Sandler, 2003).

TEM images of the CNT network in the epoxy matrix were prepared for the aligned CNT's. Figure 27 shows this network, and helps outline the problems with random oriented CNT's and the creation of backscattering of the electrons through the composite. TEM was utilized to show all the CNT's through the materials cross-section, and while one isn't able to see if the CNT's are touching in the vertical plane, you are able to see the curvature, electron back scattering, and voids that are often present in CNT filled composites.

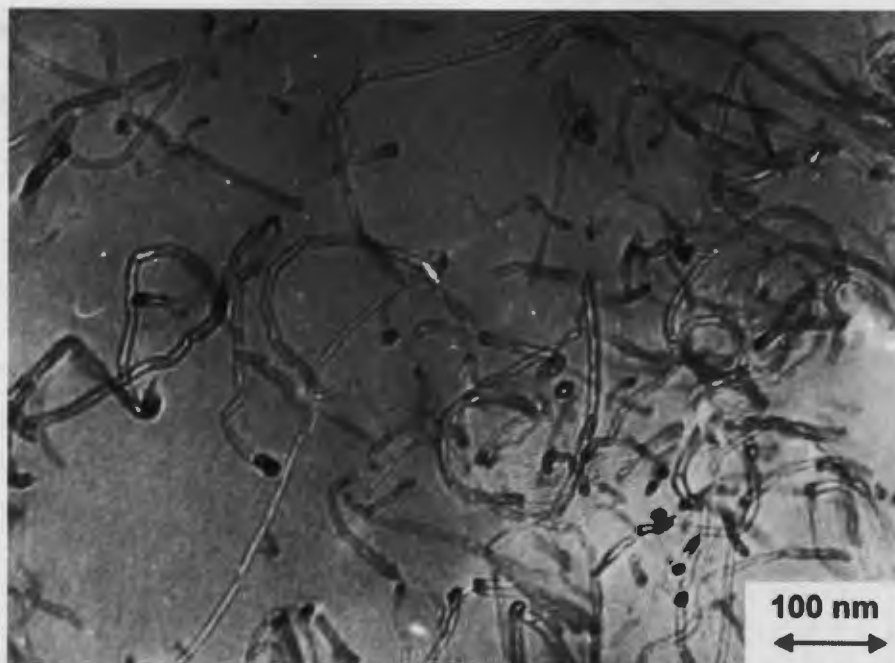


Figure 27: TEM image of a CNT percolating network in an epoxy matrix (Schaffer & Sandler, 2003).

When CNT processing and manufacturing had progressed to the point of being able to provide large numbers of SWCNT's, researchers began researching metal replacement opportunities. Research included both conductive polymers and traditional thermoplastics. One paper by McLaculan (2005) investigated early modeling of percolating networks of SWCNT's. The resistivity versus volume fraction of SWCNT's in a polyamide matrix is shown in Figure 28, and while the percolating network modeling is useful for analysis of future research, the composites in the study did not obtain conductivities high enough to be useful for a metal replacement application.

Research by Gao et al. showed that production of aligned SWCNT's is possible, and that the CNT's can be transferred to a gold nano-platelet for further processing (Gao et al., 2000). The aligned SWCNT's are shown in Figure 29, and hold many possibilities in creating light flexible electronic components. Additionally, thermo-processed synthetic

metals could achieve preferential alignment along the conduction path with proper tool design and processing.

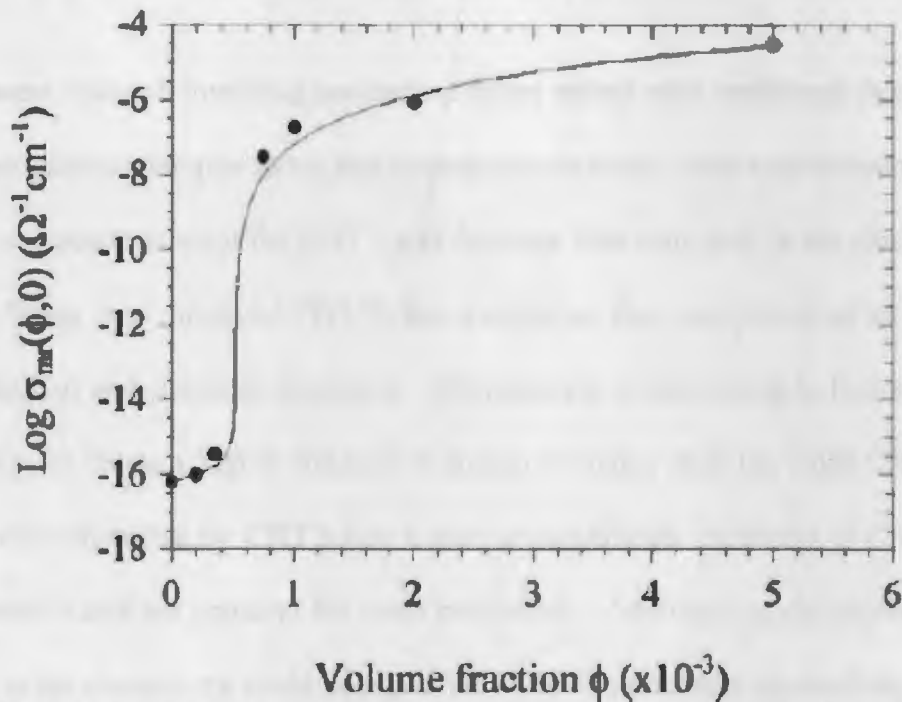


Figure 28: Resistivity of polyamide-SWCNT composite for various volume fractions (McLaculan, 2005).

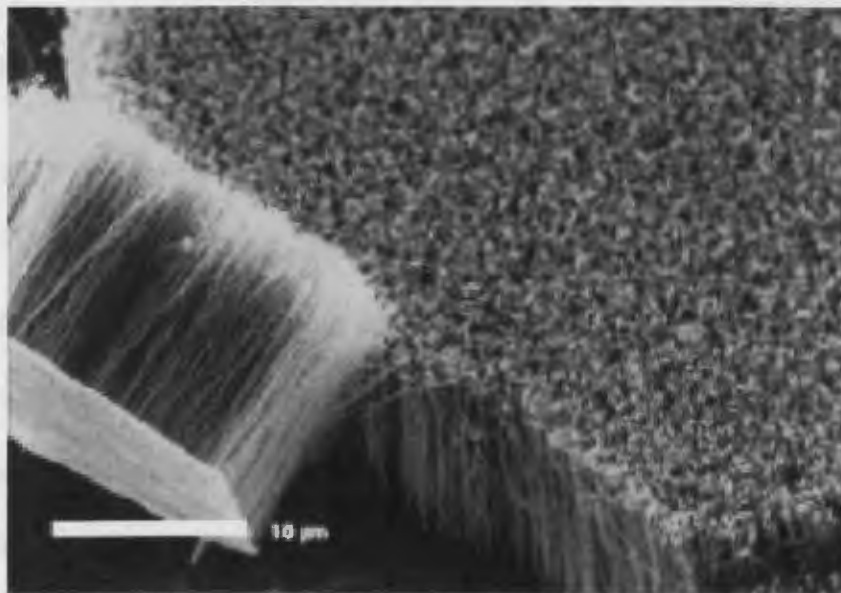


Figure 29: Aligned SWCNT's grown on a silicon wafer and transferred to a gold platelet (Gao et al., 2000).

The possibility of a highly conductive, flexible composite holds many possibilities for practical applications, including flexible electronics. Imagine an Ipad™ that is as thin as a sheet of paper and can be folded and placed in your pocket.

Recent research involving conductive fillers mixed with traditional thermoplastics include secondary techniques to try and increase conductivity. One such technique is stretching the composite to align the CNT's and decrease backscattering of the electrons. Research by Wang et al. involved CNT/Nylon composites that were stretched to investigate both mechanical and electrical properties. The researchers were trying to find a more economical way to create a highly conductive composite rather than the solid CNT method, which involves spinning the CNT's into a yarn or nanothread. Spinning of CNT's is still quite expensive and not practical for mass production. Additionally, the solvent method, according to the researchers, could only provide limited increases in conductivity when wet spinning the solution, due to the need for shorter CNT's. The researcher's solution involved an improvement to the dry method by creating an unwoven CNT ribbon, then casting the ribbon layer by layer in a composite structure.

The CNT ribbon itself was unique, as it was created via the aligned CNT method previously outlined above. Long, aligned CNT's with an average length of 700 μ m were pulled into thin aligned ribbons (Wang et al., 2011). These thin ribbons were then infused with a nylon 66/phenol solution and layered to create a composite that was 10cm long, .5cm wide and 20 μ m thick (Wang et al., 2011). The composites were then stretched for 2%, 4%, and 7%, and tested against unstretched composites for both mechanical and electrical properties. The researchers found significant increases in mechanical properties, but

this paper will focus on the electrical advantages. Figure 30 shows the various composites. Figure 30a shows the CNT ribbon as created, and b shows the results of stretching. Figure 30c is the composite as created, d is 2% stretching, e is 4% stretching, and f is 7% stretching (Wang et al., 2011).

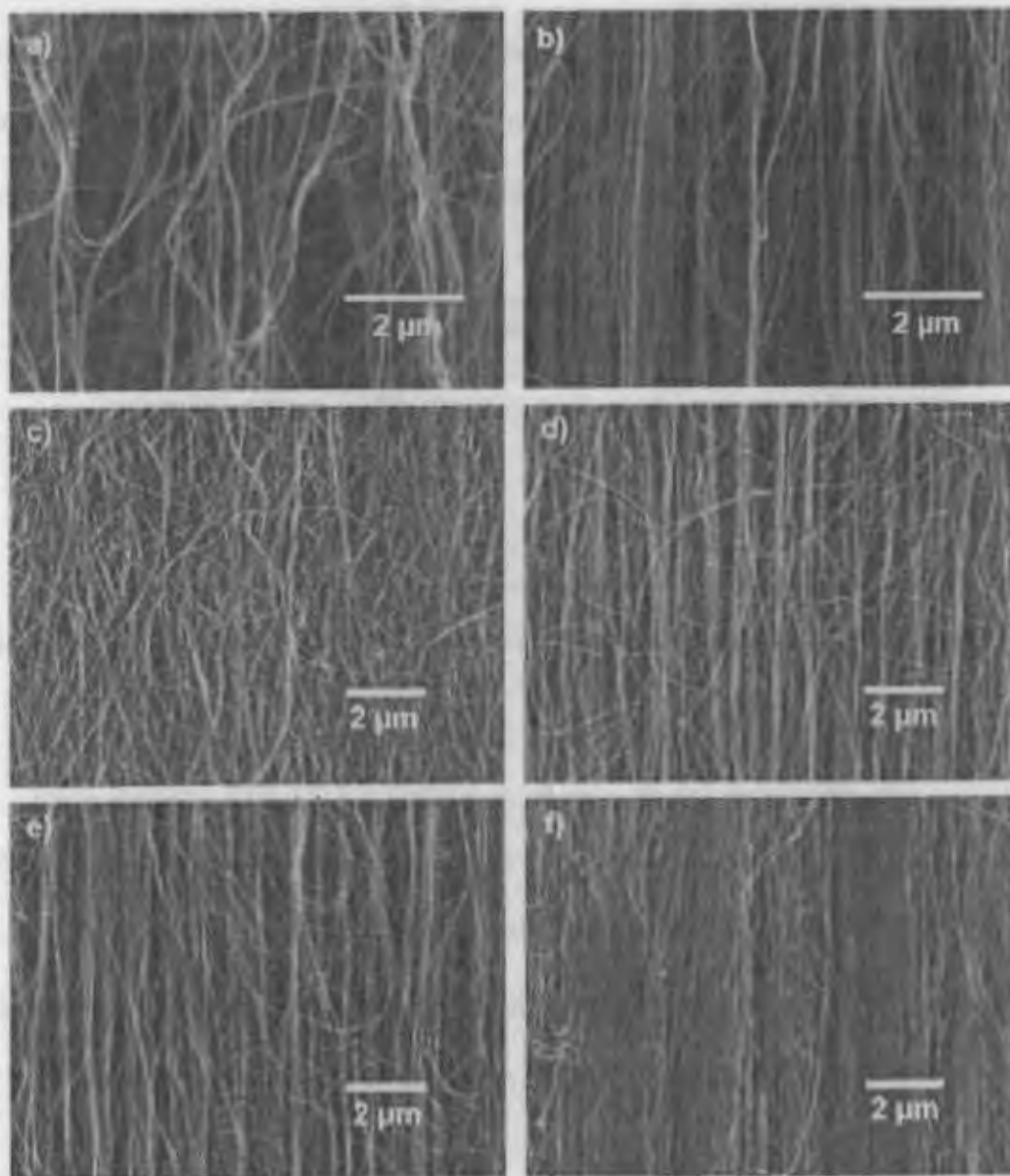


Figure 30: CNT alignment for various stretch ratios. Figure 30a shows the CNT ribbon as created, 30b shows the results of stretching. Figure 30c is the composite as created, 30d is 2% stretching, 30e is 4% stretching, and 30f is 7% stretching (Wang et al., 2011).

Table 3 outlines the increases in both mechanical strength and electrical conductivity for the various stretch ratios. The ribbon as created had a conductivity of 520 S/cm, which is three orders of magnitude lower than pure copper, but high enough to conduct significant current. The highest conductivity was reached by the 7% stretched composite, at 417 S/cm. While this conductivity is high enough to consider this material as a metal replacement for certain electrical applications, its manufacturing method was quite cumbersome and its CNT content is very high, making this composite expensive. Additional research into economical manufacturing would be required to make this material realistic.

Samples	Tensile strength (MPa)	Young's modulus (GPa)	Conductivity (S/cm)
Pristine CNT ribbons	92	3	520
Neat nylon 6,6	44	1.6	2.0×10^{-15}
0% S-CNT/nylon 6,6	215	14	136
2% S-CNT/nylon 6,6	318	21	185
4% S-CNT/nylon 6,6	540	43	335
7% S-CNT/nylon 6,6	625	56	417

Table 3: Mechanical and electrical properties of stretch aligned CNT/Nylon66 composites (Wang et al., 2011).

Early research with CNT's utilized unsorted SWCNT's, and one very detailed and meticulously documented experiment included Polyaniline and SWCNT's prepared with various CNT weight percent fills. This research was carried out early in CNT composite development and outlines some very interesting properties and shows some challenges that need to be overcome to create a true conductive metal replacement composite.

Research by Ramamurthy et al. (2004) involved using polyaniline and SWCNT's created by electric arc discharge. This research was of interest because it was so well documented that it could easily be repeated to verify results. The paper meticulously noted

all the parameters and procedures for sample creation and testing. The results also created additional questions that would need to be investigated in future research.

The polyaniline in this research was oxidized into an emeraldine salt and then deprotonated into an emeraldine base. As was previously discussed, this adds soliton sites to the polymer chain and changes its method of conduction, increasing the conductivity. The CNT's were sonicated and various weight percents were mixed with polyaniline in a solvent solution of DMPU. The solvent was then removed under vacuum at a temperature of 50C (Ramamurthy et al., 2004). The resulting films of polyaniline and SWCNT's were then tested for their electrical properties.

Figure 31 shows the resulting conductivity for the films versus CNT weight percent. The conductivity for ps-1 was 1100 S/m, which was neat polyaniline, and reached 2300 S/m for 10% weight of SWCNT filler. A conductivity of 10,000 S/m minimum would be required to consider a material as a metal replacement.

Figure 32 shows voltage versus current for the various composites. As the weight percent of CNT's increases, so does the current carrying capacity of the film. This is intuitive, but the interesting characteristic to note is the nonlinear voltage-current curve. The neat polyaniline has a curve like a semiconductor, where a voltage threshold must be met for significant current flow. As the percent of CNT content increases, the current carrying capacity of the composite increases, along with the composites conductivity. The phenomenon of interest occurs at 10% wt CNT content, where a percolating network of conductive CNT's is formed between 5% wt and 10% wt. Previous work has typically shown a percolating network of CNT's is created between .1% and 5% wt, and this is shown to be

the case based on Figures 25, 26, and 31 (Ramamurthy et al., 2004) (Schaffer & Sandler, 2003). However, the nonlinear regions of the current-voltage curves show that while a percolating network is formed, a percolating network of *conductive* CNT's isn't formed until 10% wt of CNT. The linear current-voltage curve for 10% wt is desirable from an electronics standpoint.

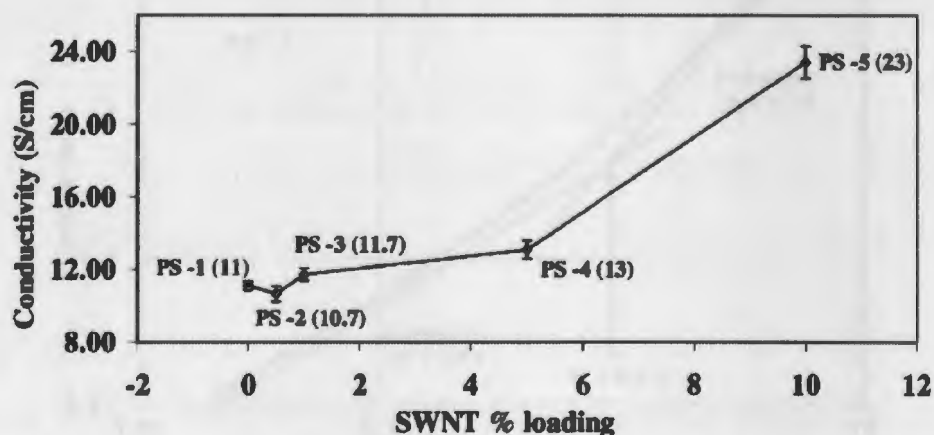


Figure 31: Conduction of polyaniline composite versus weight percent fill of SWCNT's (Ramamurthy et al., 2004).

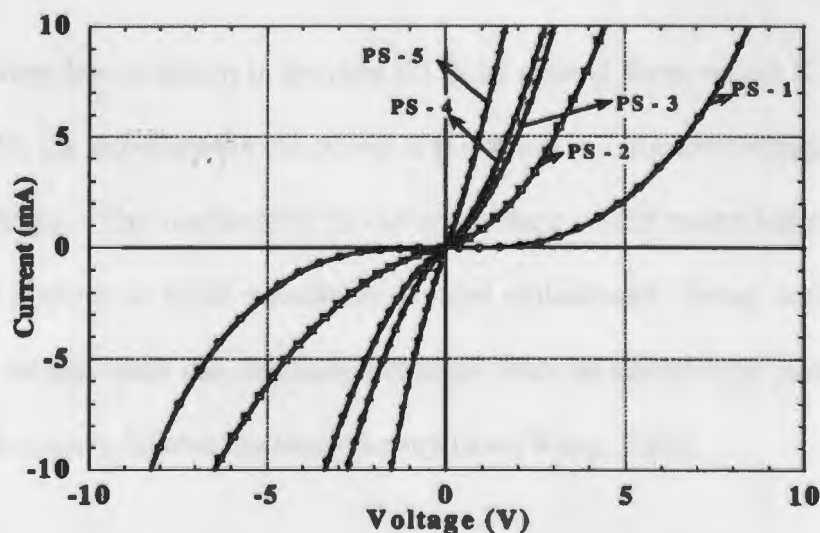


Fig. 2. $I-V$ characteristics of PANI/SWNT devices.

Figure 32: Current-Voltage curves for polyaniline/CNT composites (Ramamurthy et al., 2004).

The current-voltage curve for .5% wt of CNT content is replotted on a log-log scale to help highlight the nonlinear region of the curve in Figure 33. The log-log scale helps emphasize the nonlinear portion of the curve and help fit a power law curve on top of the data.

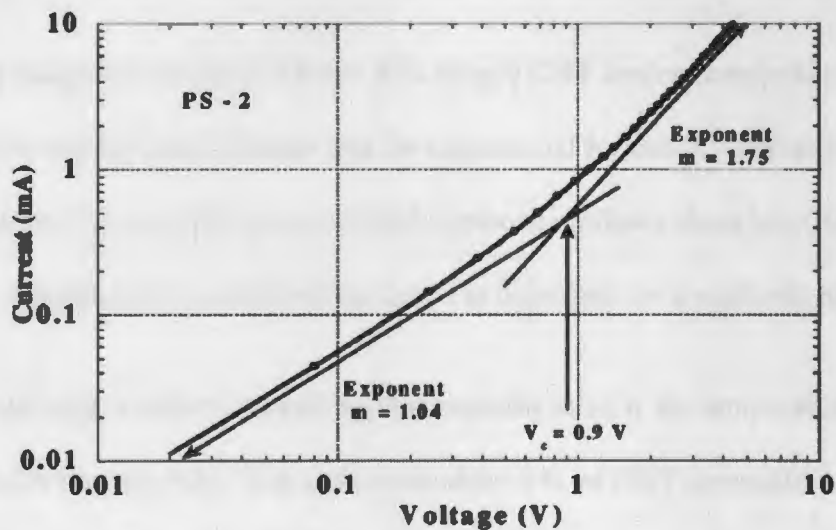


Figure 33: Log-Log plot of the current-voltage curve for .5% wt CNT content (Ramamurthy et al., 2004).

The power law is shown in formula (2) in its general form, where K is a constant. From Figure 33, the exponent for the power law is close to 1 for low voltages, but is 1.75 for higher voltages. The nonlinearity in current-voltage would create issues with instrumentation and sensors, so is not suitable for a metal replacement. Issues would be created at the critical voltage when the conduction changes from an Ohmic type material to a material that more closely follows the Mott-Gurney Law (Wong, 2010).

$$I = K * V^m \quad (2)$$

The exponents and critical voltages for the remaining composites are shown in Table 4.

Composite sample	Approximate voltage range (V)	Power law exponent	Correlation coefficient	V_c (V)	Approximate voltage range (V)	Power law exponent
PS-2	0.02–0.3	1.05	0.99951	0.9	1.7–4.5	1.76
PS-3	0.02–0.3	1.02	0.99959	0.6	0.8–3.1	1.49
PS-4	0.02–0.3	1.04	0.99974	0.5	0.8–2.8	1.41

Table 4: Power law exponents for PANI-CNT composites with .5%, 1%, and 5% wt CNT content (Ramamurthy et al., 2004).

The voltage-current curve for the 10% weight CNT content composite is shown in Figure 34. The log-log plot indicates that the exponential for this I-V curve is 1.08, which indicates that the 10% wt CNT content PANI composite follows ohms law (Ramamurthy et al., 2004). A predictable current-voltage curve is important for a synthetic metal.

The last topic covered in detail by Ramamurthy et al is the temperature dependence of the PANI-CNT composites. The author chose the 1% wt CNT composite to publish temperature dependence results, but states that the 5% and 10% wt composites had similar results. The 1% wt CNT composite's temperature dependence can be seen in Figure 35.

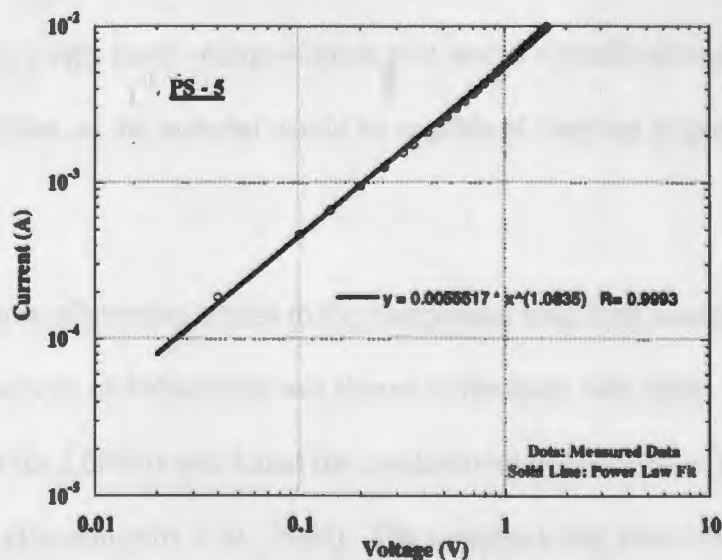


Figure 34: Log-Log plot of voltage-current curve for 10% wt CNT's (Ramamurthy et al., 2004).

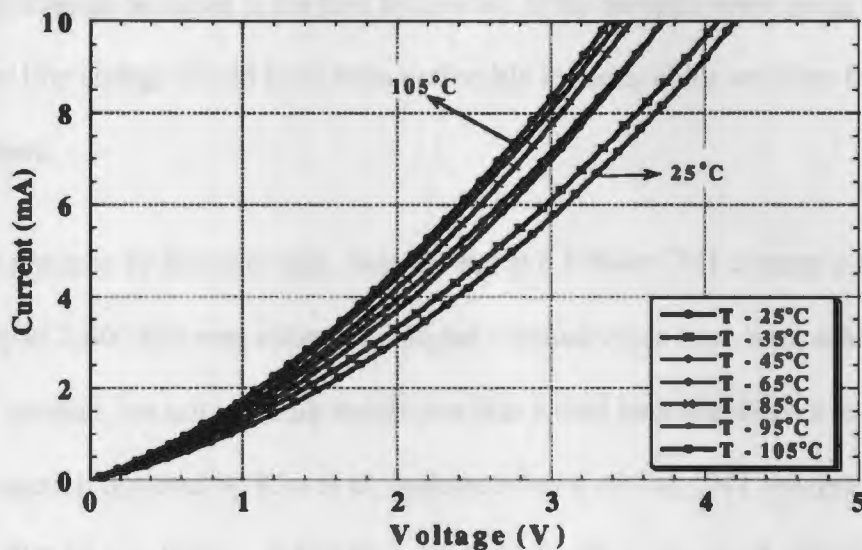


Figure 35: Current-Voltage curves at various temperatures for the 1%wt composite (Ramamurthy et al., 2004).

The temperature dependant results create an interesting new problem for metal replacement. A wire harness in an engine compartment can easily see a temperature range of -40C to 90C, and a change in the current-voltage characteristics of the conductive material could create changes in sensor readings and electronic component behavior. However, the temperature dependent behavior becomes less important as the conductivity of the material increases. Ideally, a very steep voltage-current plot would virtually eliminate the temperature dependence issue, as the material would be capable of carrying large currents at low voltages.

The last item of mention relates to the composites long term conductive stability. Long term conductivity of Polyaniline was shown to fluctuate with time. The research tested 30 samples for 2,000hrs and found the conductivity to be stable in the samples that contained CNT's (Ramamurthy et al., 2004). The samples being tested to roughly the age of 3-months is consistent with the findings for neat polyaniline where the majority of the

conductivity change occurred in the first 6-months. If the samples were going to change conductivity, the change would have been noticeable in the 2,000hr test time frame used by the researchers.

The research by Ramamurthy, showed that at a 10%wt CNT content a maximum conductivity of 2,400 S/m was achieved. Higher conductivities have been achieved with lower CNT content, but not utilizing techniques that would lend themselves to mass production. Research reported by Kim et al. indicated that a .4% wt CNT content solvent mixed into PMMA resulted in a 3,000 S/m conductivity (Spitalsky et al., 2010). Koerner (2010) utilized polyurethane and MWCNT's to achieve a conductivity of 2,000 S/m at a CNT content of 27% wt, but the material was again solvent cast (Spitalsky et al., 2010).

One way to further increase CNT composite conductivities are to create free radicals on the surface of the CNT's that interact with the polymer conducting matrix. Typical research utilizes acid functionalization, and the majority of this research is to create a rough CNT surface that mechanically bonds to the polymer matrix for reasons of improving the strength of the composite. A new paper by Yang et al. utilized plasma functionalization of CNT's to create oxygen induced free radicals on the surface of the CNT's which would interact with a PANI matrix to increase conductivity.

Yang et al. (2010) varied the argon plasma parameters to try and optimize the plasma process for maximum conductivity. Figures 36 – 40 show the effects of the various parameter modifications on conductivity. The composites were all in situ polymerized, in other words, the CNT's were dispersed in the monomer liquid, and then the polymer was polymerized around the CNT's. This resulted in good CNT distribution.

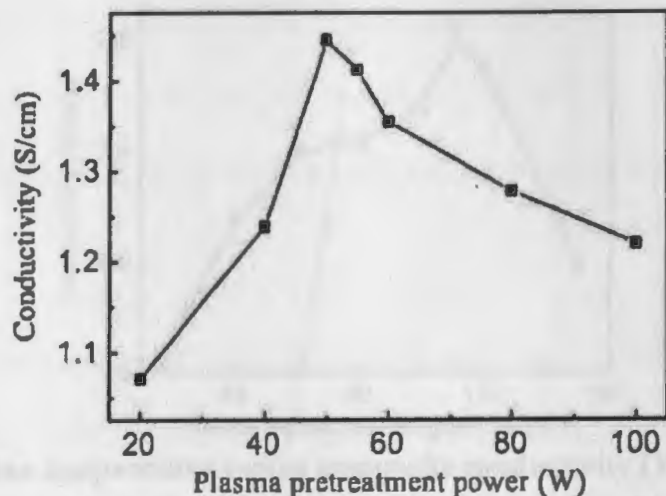


Figure 36: Plasma RF power versus composite conductivity (Yang et al., 2010).

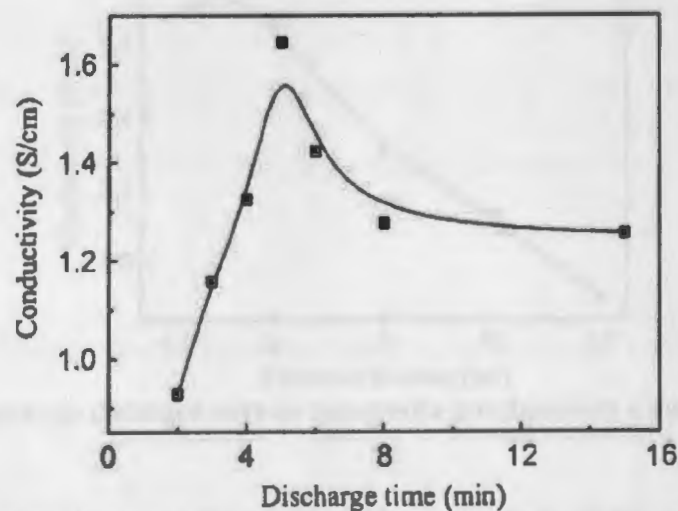


Figure 37: Plasma discharge time versus composite conductivity (Yang et al., 2010).

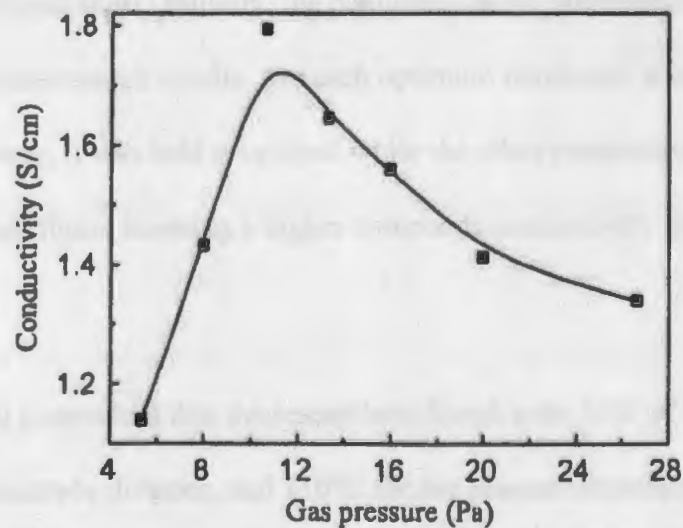


Figure 38: Plasma gas pressure versus composite conductivity (Yang et al., 2010).

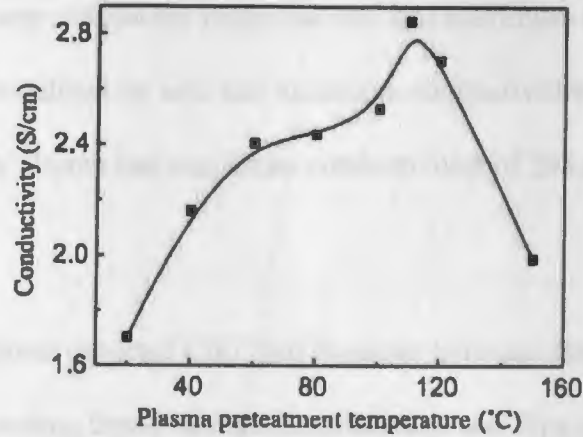


Figure 39: Plasma temperature versus composite conductivity (Yang et al., 2010).

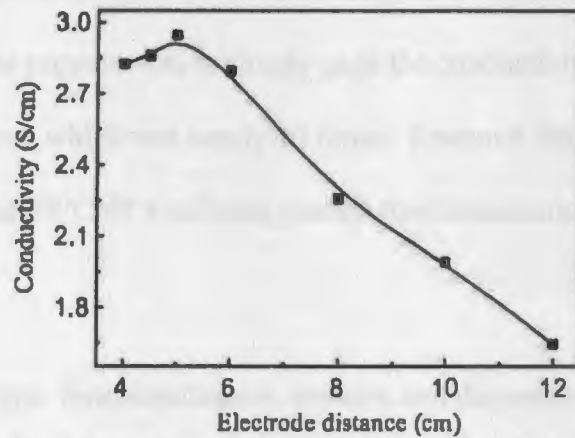


Figure 40: Electrode distance versus composite conductivity (Yang et al., 2010).

In each instance the researchers held all the parameters steady and varied just the parameter under investigation. Initially, the parameters were optimized based on literature research and previous research results. As each optimum parameter was found, starting with plasma RF power, it was held at optimal while the other parameters were varied. This is the reason for each figure showing a higher composite conductivity over the previous figure.

The optimal parameters that the researchers found were 50W of RF power, 13.3Pa of pressure, 5cm electrode distance, and 110°C for the plasma temperature (Yang et al., 2010). The researchers found that under the same polymerization conditions and CNT con-

tent, composites that were not plasma functionalized had maximum conductivities of 29.9 S/m, and CNT's functionalized by acid had maximum conductivities of 93.6 S/m, while those functionalized by plasma had maximum conductivities of 294.6 S/m (Yang et al., 2010).

Yang, et al. utilized unsorted CNT's of diameter between 20nm and 30nm. As was previously discussed, sorting based on diameter, chirality, and Single-Walled CNT's would increase conductivity of the composite. Additionally, the researchers did not use a highly doped Polyaniline. The purpose was to simply gage the conductivity increase due to the plasma functionalization, which was nearly 10 times. Research into a superconductive composite of PANI and SWCNT's utilizing plasma functionalization would be excellent future research.

Besides CNT type, functionalization, content, and dispersion techniques, research into CNT orientation has also been performed. Sharma, Tripathi, and Vijay tried using a magnetic field to preferentially align CNT's in a polycarbonate matrix to create a percolating network at low weight percent fill of CNT's. This research was geared toward creating a low cost and effective EM shield, but could also be utilized to create a highly conductive polymer by preferentially aligning the CNT's. The researchers used polycarbonate due to its amorphous and glassy nature. Crystalline polymers can create regions of crystallinity without any CNT content, so PC was chosen as a polymer carrier for the CNT's. Sorted CNT's were used, via SWCNT's and MWCNT's to see which reacted more favorably to the preferential alignment. The researchers used solvent casting method via dissolving the

polycarbonate in benzene and ultrasonication to disperse .1% of each CNT class (Sharma et al., 2010).

The results shown in Figure 41 indicate that at .1% wt CNT's, both the SWCNT and MWCNT composites did not create a percolating path when not subjected to the magnetic field. When measured along the direction of the magnetic field, the dielectric constant of the composite showed significant increases over the composites without preferential alignment. Figure 42 shows the current-voltage, characteristics for the preferentially aligned composites.

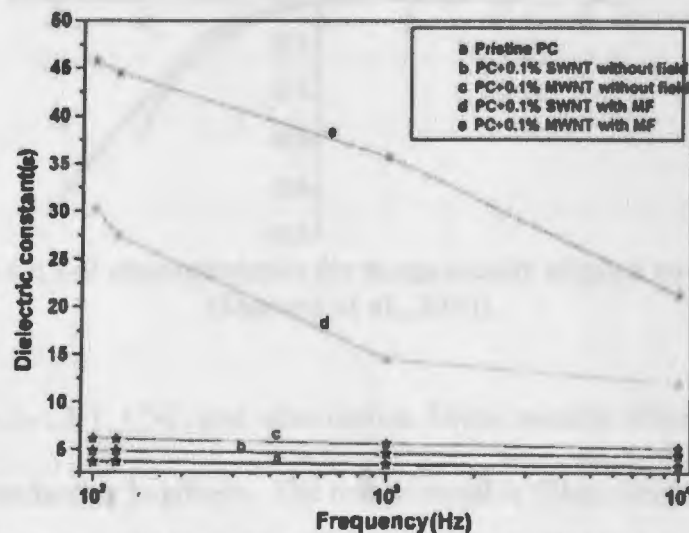


Figure 41: Dielectric constant versus frequency (Sharma et al., 2010).

Figure 42 indicates that the SWCNT composite did not align as well as the MWCNT composite. There are multiple possible reasons for this. First, as was covered in the previous section on CNT's, only metallic SWCNT's react to magnetic fields, and secondly only 1/3 of SWCNT production is generally metallic. On the other hand, while MWCNT's conductivity is highly dependent upon its outer shell, it still contains inner shells that react to the magnetic field, and that conduct in some manner. For these two main

explanations, it is the author's belief that this is the reason the MWCNT composite exhibited more linear I-V behavior, indicating a percolating network. An interesting variation to this research would be to sort metallic SWCNT's for use in preferential alignment.

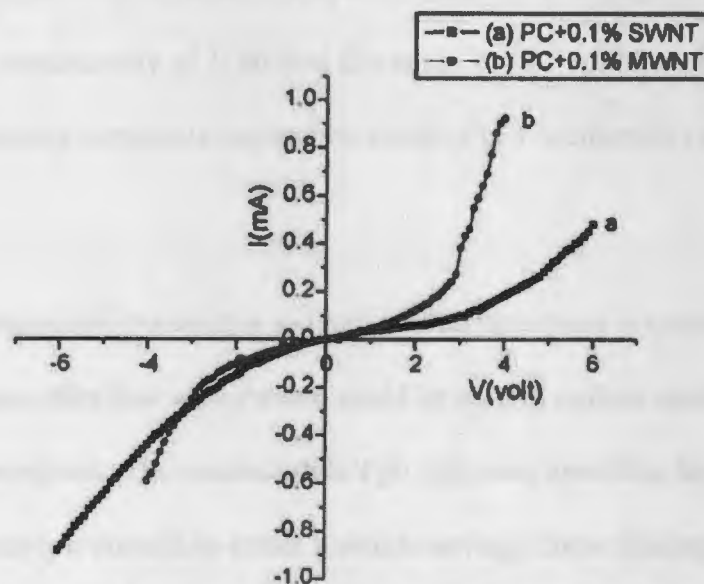


Figure 42: I-V characteristics for magnetically aligned composites (Sharma et al., 2010).

In addition to CNT, CNF, and other carbon fillers; metallic fillers have also been used to enhance conducting polymers. The reason metallic fillers were investigated was mainly due to cost and processability. Metallic fillers are less prone to degradation due to thermo processing techniques, and are also resistant to solvents. They are able to interact with the conductive domains on the polymer chains and, when used in fiber form, create conductive percolating networks. One downside is that metallic fillers in their least expensive form, powdered, do not provide good aspect ratios for a conductive percolating network. They also tend to react poorly to humidity and as they age, have a marked reduction in conductivity due to oxidation (Wu et al., 2007).

One such research dealing with metallic filler involved the addition of gold nanofibers into polyaniline. The PANI used in the research had an as produced conductivity of 2 S/m, but after the addition of the gold nanofibers, the conductivity was increased 50 times (Lu et al., 2011). The research also included doping and casting the PANI into nanofibers. It was found that nanofibers of doped PANI were much more conductive than bulk doped PANI, reaching a conductivity of 3140 S/m (Lu et al., 2011). Additionally, adding gold nanofibers and creating composite nanocables resulted in a conductivity of 7720 S/m (Lu et al., 2011).

The gold nanocable research is a significant advancement in conductive composite research. The nanocables that were created could be used to replace standard copper or aluminum wire harnesses. The research didn't go into mass specifics, but if the wt% of the gold nanofibers was low enough to create a weight savings, these findings have important implications to the automotive industry's constant search for weight savings and consequent fuel economy increases.

A novel paper focused on metal filler outlined research into a polymer/eutectic metal based thermally processable material, and provided the frame work for a possible candidate for industrial vehicle electrical systems. Unfortunately, it has a number a drawbacks including a high content of eutectic metal filler. However, the material was easily able to be thermally processed due to the low melting point of the eutectic. Mrozek et al. (2010) set out to search for an alternative to metal filled polymers, which are typically heavy and very viscous due to the metal filler, and inherently conductive polymers, which typically require high processing temperatures to obtain resin melt. These high temperatures are of-

ten near or at the thermal degradation temperature due to the stiff, stable aromatic backbones in the polymer chains. Previous attempts to utilize a low melting temperature eutectic failed, due to the eutectic not dispersing well in the polymer, creating an overall conductivity of 10^{-17} s/cm (Mrozek et al., 2010).

Mrozek et al. (2010) found a way to better disperse the eutectic via the addition of nickel particulate filler. The nickel filler prevented coalescence of the eutectic. The researchers held the nickel content loading constant at 10% to prevent the high viscosities seen in typical metal loaded polymers. The eutectic loading was varied between 30% and 60% for the test samples, which were all prepared in a single screw extruder per Table 5. Polystyrene was utilized as the polymer carrier due to well characterized viscosity which would be beneficial to future research on viscosity changes for the various metal contents (Mrozek et al., 2010). The eutectic metal utilized was a 58% Bismuth and 42% tin and had a melting temperature of 138°C, which is less than the processing temperature for the grade of polystyrene chosen at 260°C (Mrozek et al., 2010).

Figure 43 outlines the conductivity for the overall metal content. One can easily see that the conductivity increase between a 50% and 60% loading is minimal. A well connected conductive network seems to form around a 50% loading, but the researchers outlined that the conductivity levels off 60% at 350 S/cm. As was previously mentioned, a conductivity of 100s/cm would be required to consider a material for a metal replacement, and this eutectic/polymer composite is three times that conductivity. This material appears to be an excellent candidate for the connector application to be discussed shortly; however, no research was performed on conductivity versus age, or the materials ability to withstand

harsh environments or oxidation. This research, in addition to research into its mechanical properties, would be required before this material could be considered for a practical application.

Total metal content (vol%)	Nickel (vol%)	Eutectic (vol%)	Polystyrene (vol%)
30	10	20	70
40	10	30	60
50	10	40	50
60	10	50	40

Table 5: Total metal content for the composite test samples (Mrozek et al., 2010).

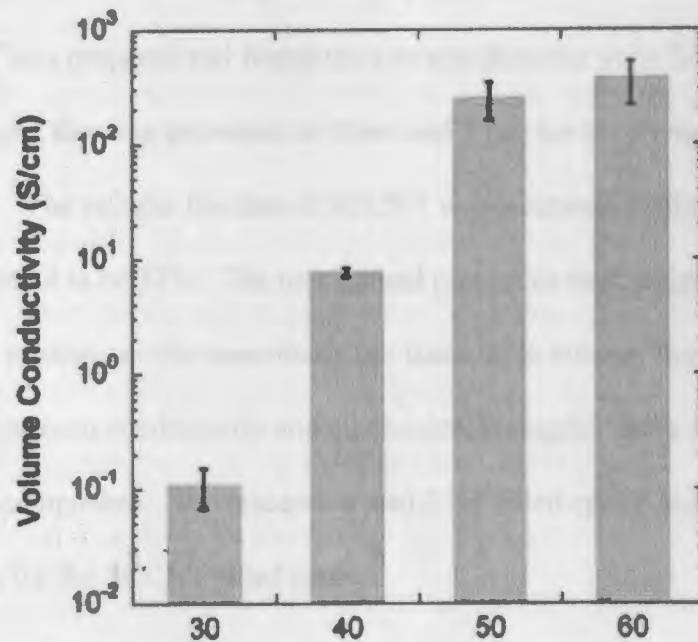


Figure 43: Conductivity per metal loading content for each eutectic composite (Mrozek et al., 2010).

An investigation into a replacement for lead based solder directly relates to this paper's investigation into a material for use in industrial vehicle electrical systems. The requirements are nearly the same for both applications, including high mechanical strength, and time stable conductivity. Wu et al. investigated a new material that was a polymer based conductive adhesive for use as a solder replacement. Previous attempts have had

limited success due to metallic filler's sensitivity to temperature and humidity aging (Wu et al., 2007). The solution that was investigated was to coat carbon nanotubes in silver. The idea was the carbon nanotubes provide high aspect ratios and the potential to create a good conducting network, while the silver coating would provide better conductive contact and would overcome the conductive limitations of semiconducting CNT's.

Wu et al. silver coated bulk CNT's via chemical plating by utilizing silver nitrate. The silver coated carbon nanotubes (SCCNT), were then ultrasonically mixed with epoxy resin to create an uncured resin ready for use as a polymer based solder. The researchers reviewed the CNT's as prepared and found the average diameter to be 20nm and the average length to be 5 μ m, this was increased to 30nm and 5 μ m for the silver coated nanotubes (Wu et al., 2007). The volume fraction of SCCNT was increased until the conductivity peaked, this was found to be 31%. The mechanical properties took a significant decrease after 28% volume fraction, so the researchers felt that a 28% volume fraction would be the best compromise between conductivity and mechanical strength. Table 6 outlines the results of the epoxy composites. The research tested CNT filled epoxy and silver filled epoxy as baselines for the SCCNT filled epoxy.

Wu et al. showed that the CNT filled epoxy had the lowest conductivity at 276 S/cm followed by the silver particle filled epoxy at 4237 S/cm. The highest conductivity is attributed to the SCCNT epoxy at 4524 S/cm. While this conductivity increase isn't huge, the reduction in mass is very significant. In addition to the weight savings, the SCCNT composite showed significant age stability. The SCCNT composite showed about a 15% decrease in shear strength and conductivity in its aged form, while the silver filled compo-

site showed a 200% decrease in conductivity and a 35% decrease in shear strength (Wu et al., 2007).

Conductive fillers	CNT	SCCNT	Silver particles with 1 μm diameter size
Bulk resistivity ($\Omega\text{ cm}$)(Cu electrode)	3.62×10^{-3}	2.21×10^{-4}	2.36×10^{-4}
Shear strength (MPa)			
Cu substrate	18.7	18.6	10.6
Al substrate	19.6	19.6	11.9
Volume fraction of filler (%)	28	28	28
Mass fraction of filler (%)	15	41	67

Table 6: Electrical and mechanical properties of conductive filled epoxy composites (Wu et al., 2007).

Besides the eutectic/polymer blend, I was unable to find research that pertained to a highly conducting thermally processable composite. Some research into carbon nanofiber composites alluded to thermally processable composites, but did not provide details into processing or overall conductivity. It only provided the drawbacks, mainly that CNF's break during high shear mixing, resulting in shorter fibers and a larger CNF loading to create a percolating network.

Researchers typically utilize solvents because solvent processing provides a quicker and simpler path to producing test samples. First, solvent processed conductive polymers can be doped through the solvent. This creates a uniform and highly doped polymer matrix. The second reason solvent processing is preferable is that CNT's and other fillers can more easily be dispersed in a low viscosity polymer solvent solution than in a thermally processed polymer. The last reason solvent processing is used is due to cost and complexi-

ty. Mixing a polymer in a solvent is much easier and less expensive than having to purchase equipment to thermally process the polymer and mix the filler into the matrix. The composites then have to be thermally processed in an extruder or injection molder rather than evaporating the solvent. Equipment and tools to thermally process polymers and composites can be quite expensive. Future research would need to involve thermally processed highly conductive composites in order to explore the commercial viability of synthetic metals for wire harnesses and connectors.

3. CASE STUDY

3.1 Industrial Vehicle Electrical Systems

Industrial vehicles are typically used in harsh environments that can include acids, alkalis, chemicals, fuels, oils, and salts. These harsh environments can be found in agricultural, ranching, demolition, specialty manufacturing, highway maintenance, and many other industrial applications. The chemicals found in these applications can be highly corrosive to the metal components of the industrial vehicle. A significant amount of money is spent on protection of the metals found in industrial vehicles. Special paints and protectants, like chrome plating, are used to protect the structures that perform the work and protect the occupants. Special blends of polymers are used to ensure integrity of hoses and tanks, and seals or double seals are used at every connection and join, including electrical connections.

Electrical connectors are one such system that requires robust, highly engineered parts with multiple seals to ensure electrical system integrity. Despite the attention given to the electrical connectors, there are still periodic failures due to the harsh environment and large vibrations and thermal variations seen by the electrical system. Figure 44 shows a two pin Deutsch connector that is commonly found on industrial vehicles.

Connectors such as the ones depicted in Figure 44 utilize double seals for the connector pins and single high integrity seals where the wires enter the connector. The pins are attached to the wires via mechanical clamping. High vibrations that are often found in industrial vehicles can cause this clamped joint to sometimes fail, or the seals to leak caus-

ing pin corrosion. Additionally, the labor involved in creating the connectors on the wire harness can be quite intensive leading to a high cost. With the market going over to increasing numbers of electronic devices for not only vehicle control, but also guidance and operator entertainment and comfort, the number of connectors on a wire harness is continually increasing. This makes these connections even more critical, especially with respect to the safety aspect of vehicle control and monitoring.



Figure 44: Deutsch connectors, two pin style.

Connectors such as the ones depicted in Figure 44 utilize double seals for the connector pins and single high integrity seals where the wires enter the connector. The pins are attached to the wires via mechanical clamping. High vibrations that are often found in industrial vehicles can cause this clamped joint to sometimes fail, or the seals to leak causing pin corrosion. Additionally, the labor involved in creating the connectors on the wire harness can be quite intensive leading to a high cost. With the market going over to increasing numbers of electronic devices for not only vehicle control, but also guidance and operator entertainment and comfort, the number of connectors on a wire harness is continually increasing. This makes these connections even more critical, especially with respect to the safety aspect of vehicle control and monitoring.

Figure 45 shows a Bobcat M-Series loader harness with the proprietary controls, engine, and hydraulic portions removed. Even with roughly 40% of the harness not pictured, the purple highlighted connectors give a good indication of the complexity of electrical systems on these vehicles. The Bobcat loader is in the compact equipment segment of the market, so a wire harness for an agricultural tractor or harvester could be twice as complex with multiple times the connectors.

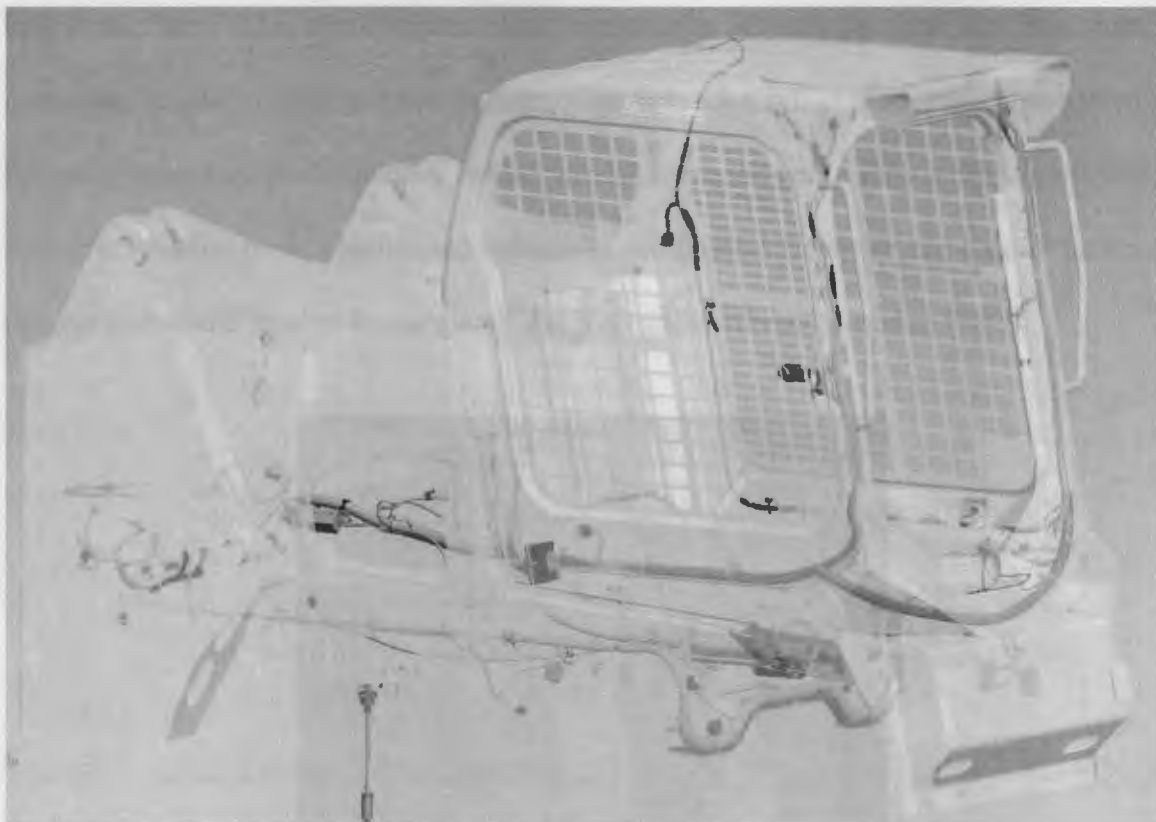


Figure 45: Bobcat™ M-Series main frame harness.

3.2 Synthetic Metals in Industrial Vehicles

If a connector could be designed to be not only more robust, but eliminated the need for multiple seals and be easier to assemble, it would be very beneficial for the industrial vehicle market. The technology could also be easily expanded to automotive, even though

that market typically only utilizes sealed connectors on the engine harness, and the connectors are not sealed to the same standards as industrial vehicles.

Additionally, fuse relay centers in industrial vehicles often have fuses that vibrate out of location causing failures. The centers are highly sealed and protected, much like the connectors. Figure 46 shows a typical fuse relay center. The fuse relay center could benefit from a synthetic metal by utilizing snap fits that could be molded integral to the fuses or fuse center itself. This would create robust connections between the fuses and fuse center, increasing reliability and machine up time. The fuse relay center (FRC) could be made in the same manner as the connectors, which will be discussed next. This would significantly reduce production time, which could reduce the parts costs. However, the cost of the synthetic metal would need to be comparable to the copper currently used in FRCs.



Figure 46: Typical fuse relay center.

Connectors could benefit from synthetic metals, but would need more engineering time and testing due to their requirements over FRC's. Currently, connectors are multiple parts, including pins, housing, wire seals, connector seals, and pin seals. The connectors could be simplified to two parts through the use of a double barrel injection molding machine and a shuttle mold.

A double barrel injection molding machine, Figure 47, is capable of injection molding two different materials. This is currently utilized in multiple applications, especially automotive where an expensive soft touch material is injection molded over an inexpensive robust material. This is known as over-molding, and is not a new concept, but by utilizing a double barrel injection molding machine the process can be completed in a single machine and in a single tool, versus multiple tools and machines.

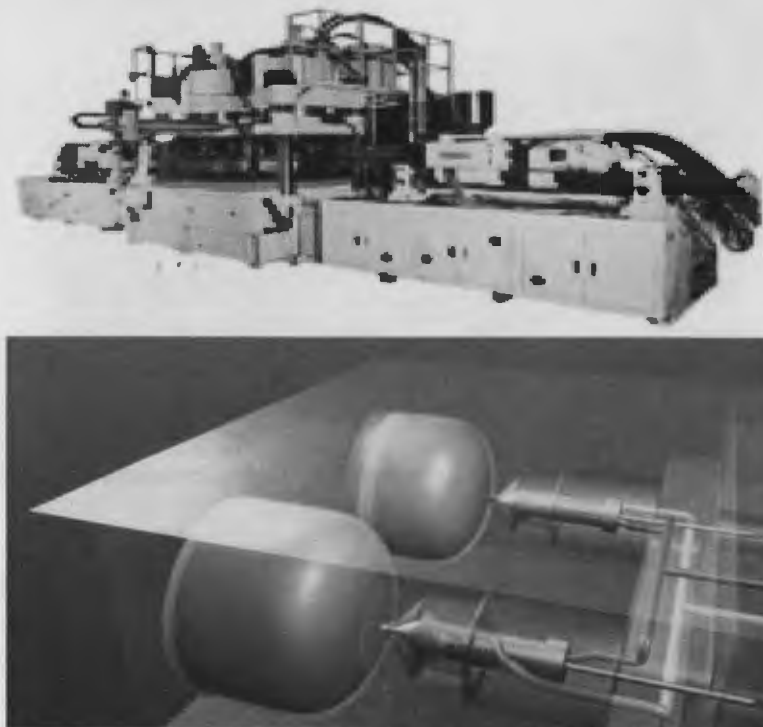


Figure 47: Double barrel injection molding machine (top) with example co-injection molding (bottom). (Bemis, 2011)

A shuttle mold is utilized to move the center core of the tool between two cavities, or co-injection can be utilized if the materials can be molded at similar temperatures. In the case of the connector, the insulating connector housing would be injection molded first. This can be a glass filled nylon 6, neat nylon 6, or polyolefin, but polyester has also been used. After the housing has been allowed to cool for a set period of time in the tool, the core would shuttle across to the second barrel of the injection molder and mate to a new cavity. The new cavity would have space for the conductive synthetic metal material, and the second barrel would inject this material into that space. The resulting part would resemble that in Figure 48. The part depicted in this figure would be that of the female half of the connector, with the insulating housing in gray and the synthetic metal portion in green.

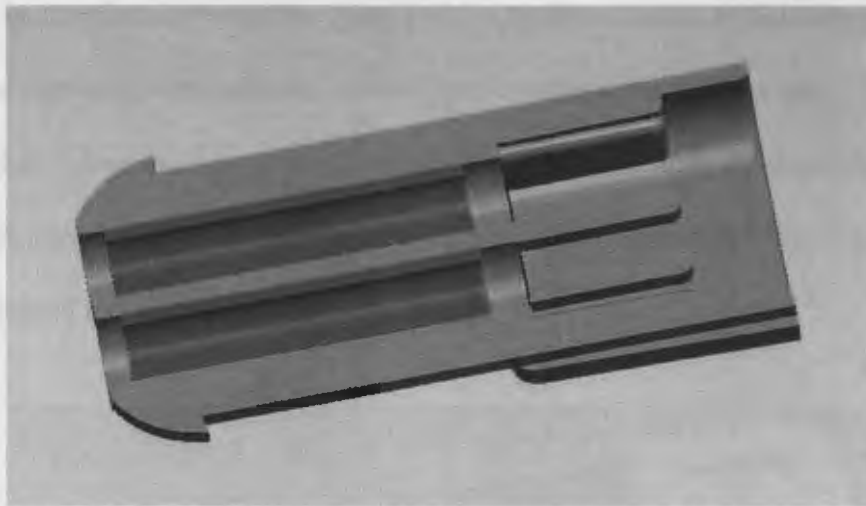


Figure 48: Female connector half, with the synthetic metal highlighted in green.

Two of the parts in Figure 48 would be required for a complete female connector. The assembly would be simpler and more robust than the current connector by utilizing a welding process. Standard welding processes like hot plate, vibration, and sonic welding could be used. However, due to the conductive nature of the synthetic metal, an induction

welding process could also be explored. Figure 49 shows the connector half with the wires placed into the proper location to bond with the synthetic metal.



Figure 49: Female connector half with the wires assembled.

At this stage a second female connector half would be placed on top and the welding process would take place. There would be no need for a wire seal, because the molten plastic from the welding process would seal the wires insulative housing to the connectors housing. The interface between the wires and the synthetic metal would also be more robust than the clamped joint currently utilized between the wires and the pins. The synthetic metal would melt into the wire strands providing more surface area for bonding and provide a higher joint strength. Figure 50 shows the connector assembly with its male counterpart assembled to form an electrical connection.



Figure 50: Cut away view of female connector with inserted male connector.

The female connector in Figure 50 depicts a cut away view for easier investigation of the interface between the synthetic metal components. A seal between the male connector's wires would not be required due to the same methods used in its assembly as the female connector. What's more, due to the accuracy and repeatability of injection molding, the pin seals could also be removed. The synthetic metal portions of the male and female connectors could be designed to have a slight press fit, which would provide a water tight seal and ensure good contact and conduction across the interface.

A housing seal may be needed in certain severe environments, but would probably not be required for most applications. The housing seal is shown in Figure 50 as three fine ribs around the housing's perimeter, but most applications would not require this seal, especially if this concept were used in automotive applications. Figure 51 shows a typical automotive unsealed connector. This style of connector is also sometimes used in enclosed cab applications as well due to the control operator environment.

In addition to electrical connectors and fuse relay centers, the research with aligned CNT's by Gao et al. could be expanded into creating wire harnesses themselves. The aligned SWCNT's grown by the research team was coated with PANI, which improved the mechanical characteristics and provided a protective coating for the CNT's. The aligned CNT's could be pulled into thin strands and coated with PANI. This would change them from nanowires to microfibers. The microfibers of CNT's could be processed more easily into a high current carrying wire harness. Such a harness would have the potential to be thinner, lighter, and more flexible than current metal wire harnesses. The weight savings

would be most significant to the automotive market where more stringent fuel economy regulations have been playing a significant role in vehicle design and weight.

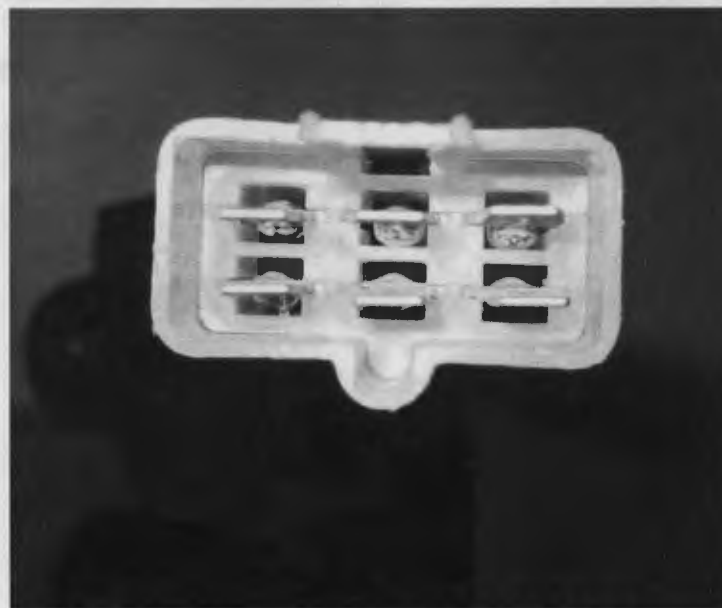


Figure 51: Unsealed connector typical of interior applications.

In addition to electrical connectors and fuse relay centers, the research with aligned CNT's by Gao et al. could be expanded into creating wire harnesses themselves. The aligned SWCNT's grown by the research team was coated with PANI, which improved the mechanical characteristics and provided a protective coating for the CNT's. The aligned CNT's could be pulled into thin strands and coated with PANI. This would change them from nanowires to microfibers. The microfibers of CNT's could be processed more easily into a high current carrying wire harness. Such a harness would have the potential to be thinner, lighter, and more flexible than current metal wire harnesses. The weight savings would be most significant to the automotive market where more stringent fuel economy regulations have been playing a significant role in vehicle design and weight.

Despite the immediate benefits of utilizing synthetic metals for current vehicle applications, there are a number of challenges that still need to be overcome before synthetic metals can become commercially viable in these applications. The next section will discuss these challenges and suggest future research to try and solve some of these road blocks.

4. FUTURE RESEARCH

4.1 Commercial Viability

There are a number of items that need to be researched before commercial viability is possible. Initially, CNT production and cost was a problem, but with each year the cost goes down with production quantities increasing. CNT's are still currently expensive, with prices hovering around \$270/lb for unsorted industrial grade CNT's. However, the high pressure carbon monoxide plasma assisted carbon vapor deposition process used by Carbon Nanotechnologies Inc has been quite successful at producing commercial quantities of CNT's. As demand for CNT's increases, and manufacturing processes become more refined, the cost will continue to fall.

Sorting CNT's is the next challenge. As was previously discussed, CNT's can be accurately sorted through a number of methods, but only ultracentrifugation appears to be able to provide significant quantities. Maybe a high composite conductivity can be reached with unsorted CNT's and highly doped synthetic metals, but the current research does not indicate this can be achieved yet without secondary processing of the CNT's. Research pertaining to high volume production of sorted CNT's would be required to move forward with commercial applications involving CNT's.

More research that utilizes thermally processed synthetic metals is required. Nearly all of the research I was able to find utilized solvent based preparation of samples. Solvent based preparation provides researchers with the best cost, ease of creation, and sample control, but does not create realistic samples for commercial applications. Research that in-

volves processing techniques that utilize mass production processes would be required to gauge the materials response and identify major processing issues and inconsistencies.

Questions such as, what happens with respect to the conductivity of highly doped PANI before and after thermal processing, is it possible to dope PANI post processing, and what role do the CNT's play in the thermal processing characteristics, all need to be addressed. Additionally, research into the crystallinity of thermally processed PANI, the effect of CNT content on crystallinity, and preferential orientation of CNT's in thermally processed CNT-PANI composites requires investigation.

Finally, research that utilizes CNT's that are sorted by metallic conduction and mixed into a highly doped synthetic metal needs to be investigated. A percolating network of metallic CNT's might be found in a lower weight percent range that can provide acceptable levels of conductivity. The current carrying capacity of such a composite would also need investigation. This could result in smaller, thinner wire harnesses which would provide a benefit to aeronautical applications as well.

5. CONCLUSION

From a practical application standpoint, synthetic metals have the potential to provide an enormous benefit to industrial vehicle electrical systems. They also have the potential to help other segments of the transportation market as well, and hold the key to creating next generation flexible electronics. Despite the immediate benefits, there is still critical research that needs to be completed before this technology is commercially viable for vehicle electrical system applications. Perhaps with continued work in this field the potential of synthetic metals can be realized in multiple applications.

REFERENCES CITED

- Abell, L., Devasagayam P., Adams N., & Monkman A.P. (1999). Crystallinity and stretch orientation in polyaniline Camphor-Sulphonic acid films. Dept of Physics, University of Durham England.
- Al-Saleh, M. H., & Sundararaj, U. (2009). A review of vapor grown carbon nanofiber/polymer conductive composites. *Carbon*, 47, 2-22.
- Arnold, M. S., Green A. A., Hulvat J. F., Stupp S. I., & Hersam M. C. (2006). Sorting carbon nanotubes by electronic structure using density differentiation. *Nature Nanotechnology*, 1, 60-65.
- Bemis Manufacturing. (2011). Advanced technology group overview. ATG.
- Dresselhaus M.S., Dresselhaus G., Eklund P.C., & Saito R. (2008). Electrons and phonons in fullerenes and carbon nanotubes. MIT, Cambridge Massachusetts.
- Endo M., Iijima S., & Dresselhaus M.S. (1996). *Carbon nanotubes*. Elsevier Science Limited.
- Epstein, A. J. (1999). Electrical conductivity in conjugated polymers. Dept of Physics and Chemistry, Ohio State University.
- Gao, M., Huang S., Dai L., Wallace G., Gau R., & Wang S. (2000). Aligned coaxial nanowires of carbon nanotubes sheathed with conducting polymers. *Angew Chemical International (1st ed.)*.
- Harris, P. J.F. (2009). *Carbon nanotube science: synthesis, properties, and applications*. Cambridge University Press.
- Hong, S., & Myung, S. (2007). nanotube electronics: A flexible approach to mobility. *Nature Nanotechnology*, 2, 207-208.
- Issi, J.P., Langer, L., Heremans, J., & Olk, C. H. (1995). *Electronic properties of carbon nanotubes: experimental results*. General Motors Research and Development Center, Warren Michigan. Retrieved February 6, 1995.
- Long, Y., Li, M., Gu, C., Wan, M., Duvail, J., Liu, Z., Fan, Z. (2011). Recent advanced in synthesis, physical properties, and applications of conducting polymer nanotubes and nanofibers. *Progress in Polymer Science*, 36, 1415-1442.
- Lu, X., Zhang W., Wang C., & Wen T. (2011). One-dimensional conducting polymer nanocomposites: synthesis, properties, and applications. *Progress in Polymer Science*, 36, 671-712.

- Mau, A. Dai, L. (2001). Controlled synthesis and modification of carbon nanotubes and C₆₀: carbon nanostructures for advanced polymeric composite materials. *Advanced Materials*, 13, 899-913. Retrieved from <http://atmsp.whut.edu.cn/resource/pdf/8523.pdf>.
- McLaculan, D. (2005). AC and DC percolative conductivity of single wall carbon nanotube polymer composites. *Journal of Polymer Science*, 43, 3273-3287.
- Mintmire J., & White C. (1994). *Electronic and structural properties of carbon nanotubes*. Naval Research, Washington DC. Retrieved from <http://www.sciencedirect.com/science/article/pii/0008622395000189>.
- Moshe, N. (1999). Novel electrically conductive injection moldable thermoplastic composites for ESD applications. *Conductive Polymers and Plastics* (pp210-217). William Andrew Publishing.
- Mrozek, R., Cole, P., Mondy, L., Rao, R., Bieg, L., & Lenhart, J., (2010). Highly conductive, melt processable polymer composites based on nickel and low melting eutectic metal. *Polymer*, 51, 2954-2958.
- Pron, A., & Rannou, P. (2002). Processable conjugated polymers: from organic semiconductors to organic metals and superconductors. *Progress in Polymer Science*, 27, 135-190.
- Ramamurthy, P., Malshe A., Harrell W., Gregory R., & Rao A. (2004). Polyaniline/single-walled carbon nanotube composite electronic devices. *Solid State Electronics*, 48, 2019-2024.
- Roth S., & Carroll D. (2004). *One-dimensional metals* (2nd Ed). Wiley-VCH.
- Rupprecht, L. (1999). *Conductive polymers and plastics in industrial applications*. Society of Plastics Engineers.
- Schopf G., & Kobmehl G. (1997). *Polythiophenes - dielectrically conductive polymers*. Springer, New York.
- Shaffer M., & Sandler J. (2003). *Carbon nanotube/nanofibre polymer composites*. Department of Chemistry, Imperial College London, and Polymer Engineering, University of Bayreuth Universitätsstrasse, Germany.
- Shama, A., Tripathi, B., & Vijay, Y., (2010). Dramatic improvement in properties of magnetically aligned CNT/polymer nanocomposites. *Journal of Membrane Science*, 361, 89-95.
- Shinar, J., Vardeny, Z., & Kafafi, Z. (2000). *Optical and electronic properties of fullerenes and fullerene-based materials*. Marcel Dekker, New York.

- Spitalsky, Z., Tasis D., Papagelis K., & Galiotis C. (2010). Carbon-nanotube-polymer composites: chemistry, processing, mechanical, and electrical properties. *Progress in Polymer Science*, 35, 357-401.
- Stejskal, J. (2002). Polyaniline, preparation of a conducting polymer. *Pure Apple Chem*, Vol. 74, No 5, pp857-867.
- Strong, B. (2006). *Plastics: Materials and Processing* (3rd Ed). Pearson, Columbus, Ohio.
- Wang, X., Bradford, P., Lui, W., Zhao, H., Inoue, Y., Maria, J., Li, Q., Yuan, F., & Zhu, Y. (2011). Mechanical and electrical property improvement in CNT/nylon composites through drawing and stretching. *Composite Science and Technology*, 71, 1677-1683.
- Wong, M. (2010). *Derivation of Mott-Gurney Law*. Retrieved from http://my.ece.ucsb.edu/mhwong/documents/thesis_app2.pdf.
- Wu, H., Wu X., Ge M., & Zhang G. (2007). Properties investigation on isotropical conductive adhesives filled with silver coated carbon nanotubes. *Composites Science and Technology*, 67, 1182-1186.
- Xavier, F., & Varma, SJ. (2010). An investigation on the high temperature response of highly conducting polyaniline films. *International Conference on Advances in Polymer Technology*. pp119-122. Retrieved from <http://psrt.cusat.ac.in/apt10/apt10CD/HTMLS/ORAL/CPO02Varma%20S.J..pdf>.
- Yang, J., Wang X., Wang X., Jia R., & Huang J. (2010). Preparation of highly conductive CNT's/polyaniline composites through plasma pretreating and in-situ polymerization. *Journal of Physics and Chemistry of Solids*, 71, 448-452.
- Yong, E. (2007). Carbon nanoscrolls to store hydrogen. *Nanotech Science*. Retrieved from <http://www.justchromatography.com/general/carbon-nanoscrolls-h2>.