Carbon Nanotube Fiber Spinning, Densification, Doping and Coating for Microcable Manufacturing

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Abstract: The unique electrical and mechanical properties of individual Carbon Nanotubes (CNTs) surpass the properties of many highly advanced materials available in industrial applications. CNTs are the most promising candidates to replace Cu, Si and Al in a large number of electrical devices as well as for electrical conduction. Most of the applications require CNT assemblies or macroscale materials, and several techniques to make CNT fibers, threads, yarns and ropes have been reported already. Efforts to improve their electrical conductivity continue, mostly through chemical doping. Some applications of these conducting CNT fibers in electronics require a layer on the CNT fiber surface for insulation and protection against mechanical tearing. Ideally a flexible insulator on the CNT fiber can allow fabrication of CNT coils that can be assembled into lightweight, corrosion resistant electrical motors and transformers. Hydrogenated nitrile butadiene rubber (HNBR) is a commercial polymer, and it provides a unique continuous and uniform coating on the CNT fibers.

Key-words: Carbon nanotube fibers, threads, yarns, coating, microcables.

1. Introduction

As of this writing, there are several approaches to making CNT fibers, including: dry spinning,[1, 2] gas phase spun,[3] liquid phase[4, 5] and electrophoresis. The predominant approach these days seems to be the gas phase fiber spinning,[3, 6] initially reported by Zhu[7] and Windle et al.[3] as it can produce 3.5 grams of CNT fiber per hour as reported by Lashmore.[8] Regardless of the spinning method, CNTs assembled into fibers have shown higher electrical resistivity[5, 9, 10] when compared to individual CNTs.[11] Researchers, attempting to improve the electrical conductivity of CNT bundles and fibers, have chemically doped CNTs with electron withdrawing and electron donating molecules and ions through exohedral doping.[12] P-type doping has been practiced with Au⁺,[13] HNO₃ and H₂SO₄[14] while N-type doping has been achieved with N₂H₄[15] and K.[12] Additionally, B and N have been used as substitutional atoms for p-type and n-type respectively.[16] Typically, their results have shown conductivity increases of one order of magnitude. In this paper, we report the complete processing cycle of CNTs; from synthesis, fiber processing, densification, and doping, towards CNT industrial applications as electrical conductors. The doped CNT fibers have shown electrical conductivities higher than their pristine counterparts, and the insulating coating has shown reasonable uniformity along the CNT fiber surface. Although electrical insulation of CNT fibers is the main goal, the polymer coating also protects CNT fibers from mechanical tearing. Further, this coating may also hold the dopant ions/molecules within the CNT fiber. The coating approach is simple, scalable, and allows
us to modify the thickness of the coating as needed, with micron accuracy.

2. Limitations of Current CNT Fibers

CNT fibers, as with many fibers in industrial applications, are the main components of textiles, yarns, ropes and cords. Unlike many of their industrial counterparts, CNT fibers are also the main component of fibers that might be used for electrically conducting applications. Although current CNT fiber spinning methods, such as gas phase fiber spinning, can produce kilometer long fibers, the technique has an inherent disadvantage, such as the presence of catalyst nanoparticles associated with the synthesis process.[16, 17] These nanoparticles reduce the CNT fiber purity, and can affect the mechanical strength of the fiber.[16] Additionally, CNT fibers produced by dry spinning methods have shown higher electrical resistivity than Cu and Al, the most commonly used metals for electron transport. The poor conductivity has been attributed to the poor packing of the CNTs within the fiber; therefore, densification of the CNT fiber is required.[18] After densification with a solvent, the CNT fiber will typically show lower resistivity and increased mechanical strength; however, these improvements are not sufficient to consider the use of CNT fibers in electronic applications. In addition to progress in enhancing CNT electrical conductivity, an insulating coating on the fiber is needed in order for these fibers to be utilized as electrically conducting microcables.

3. Microcable Manufacturing

The dry spinning method from vertical arrays of CNTs used in our studies reduces significantly the catalyst nanoparticle presence within the fiber, also it allows the preparation of CNT fibers with improved alignment of the individual CNTs within the fiber.[19] SEM images of VA-CNTs in the Figure 1a show the alignment of CNT bundles before drawing into fibers. Figure 1b shows, by TEM, examples of the CNTs which are the main components of the CNT arrays. Dry spinning from VA-CNTs was first reported by Fan et al; since then, promising industrial applications have been reported[2], such as touch screens and TEM nanogrids.[20]

Figure 1. Micrographs of CNTs used for fiber spinning and coating: (a) SEM of VA-CNTs with a height of 300 um; (b) TEM image of individual CNTs.

CNT packing improvement within the fibers was achieved by solvent densification. In solvent densification, CNT fiber is drawn from a bobbin, dipped into a solvent, and then transferred onto a second bobbin, all while applying 1% strain. Furthermore, chemical doping has been proposed as a route to boost CNT electrical conductivity. Au doping of the CNT fiber was performed, in solution, in order to increase their electrical conductivity. Finally, the polymer coating was applied by dipping the whole CNT fiber into a polymer solution, then drawing one end at a constant speed, while the polymer is deposited along the fiber at the solution interface.

3.1. Experimental

The multi-walled CNTs were synthesized according to procedures previously reported from Nanoworld Labs, that are described by Jayasinghe.[21] Typically, 2 nm Fe alloy catalyst is evaporated on a 5 nm Al_2O_3 layer supported by a SiO_2 wafer. The growth process takes place at a temperature of 750 °C. Ethylene is used as carbon source gas (300 sccm), and a small amount of H_2O vapor - carried by argon (125 ppm) - is added to the reaction chamber. Argon is used as carrier gas, typically maintained at 1080 sccm. CNT fibers are spun on a custom setup reported elsewhere,[21], with 900 rpm twisting and 10 rpm of pulling rate. Densification of the CNT fiber is performed in H_2O/acetone (4/1 ration by volume) solution at 60 °C temperature. The lower resistivity CNT threads were obtained by exohedral doping with 0.05 M KAuCl_4 aqueous solution, according to procedures described by Jarosz et al.[22] KAuCl_4 was purchased from Sigma Aldrich, and used without any additional treatment. Resistivity measurements were performed using a 4-point probe, with the four (500 μm width) electrodes assembled parallel to each
other. Voltage was measured between the inner electrodes (spaced 4 mm apart) while current was supplied through the outer electrodes (spaced 2 mm away from their correspondent inner electrode).

The polymer used for coating was Zetpol 2000 HNBR (Hydrogenated Nitrile Butadiene Rubber), from Zeon Chemicals L. P. (Louisville, KY, USA). According to the manufacturer, this polymer has 49% ACN content and Mooney viscosity of 65 (ML1+4 at 100 °C). Typically 10 g of HNBR were dispersed in 450 mL of Acetone, purchased from Sigma Aldrich, without any additional treatment. After complete dissolution of the HNBR in acetone, solvent was evaporated by continuously stirring until volume of the polymer solution is reduced by 40%. A crosslinking agent, 0.5 g of 2-5-bis tertbutylperoxy 2-5-dimethyl hexane, was then added drop-wise. After the addition of peroxide, the solution was stirred for 5 minutes, where upon the CNT thread was dipped into the solution and the coated fiber was drawn from the polymer solution at ~6 rpm constant speed. Between the collecting bobbin and the delivering bobbin, a custom miniature furnace (160°C) was placed; the freshly polymer coated CNT fiber passes through the center of the furnace, to promote the polymer curing.

3.2. Discussion

CNT fibers were spun from VA-CNT (30 μm tall) using a custom-made fiber spinning setup as shown in Figure 2a. The CNTs were grabbed from one of the edges making a film and then pulled and twisted continuously. The arrows on the drawing show the rotation direction to achieve the twisting and pulling simultaneously. Figure 2b is an optical picture of the actual VA-CNTs (1.5 inch width) during fiber spinning. The black side is the CNT array before pulling while the gray conical shape is the horizontally aligned web of CNTs that are being twisted into a fiber. Due to the small diameter and the lack of focus, the fiber that is located at the tip of the conical shape is not visible in Figure 2b. The edge of the array becomes curved during drawing presumably by a self-adjusting method where the lengths of all the strands of CNT being drawn into the thread become equal. With this drawing procedure, it is expected that the van der Waals forces and overlap of CNT to CNT would be the same in each strand and this would produce the highest strength fiber.
The resistivity of CNT fibers further decreased after chemical doping with KAuCl₄ solution in H₂O. The CNT fiber was immersed into the KAuCl₄ solution for 30 min, and the end was extracted by a mechanical motor at a constant speed. Samples of doped CNT fibers were imaged by SEM—Figure 4a—showing bright spots along the CNT fiber. We presume these bright dots are Au nanoparticles that collected during doping, as a result of Au reduction.

Electrical characterization of doped CNT fibers by 4-point probe resistivity measurements, prior to coating, reveal an order of magnitude reduction of their resistivity. Figure 4b shows electrical resistivity of as-spun and doped CNT fibers compared to Au and Cu wires with similar diameter dimensions. In order to determine electrical resistivity of CNT fibers at atmospheric pressure and temperatures we have assembled a resistivity measurement setup. A commercial 5 pin connector, typically used in computer connectors, provides equally spaced electrodes to measure electrical resistance, in a similar manner to that of the 4 point-probe. Our setup allows us to change the distance between the electrodes by multiples of 2 mm, in order to determine consistency between the measurements. The CNT fiber is attached to the metal electrodes at their contact points, using a colloidal Ag paste. The liquid form of the Ag paste avoids damaging the CNT fiber at the contact point, thereby avoiding any compression or flattening while achieving good contact. Therefore, no pressure is used to contact the sites, and the cylindrical nature of the CNT fiber is preserved. The typical resistivity of doped CNTs is 7x10⁻⁶ Ω*m, which is almost an order of magnitude lower than the 5x10⁻⁵ Ω*m that corresponds to as spun CNT fibers. Figure 4b also reveals interesting electrical resistivity results of CNT fibers reported in literature. Davis et al. reported [5] 1.2x10⁻⁶ Ω*m [23] and most recently Behabtu et al reported [17] 3.5x10⁻⁷ Ω*m [5] for single walled CNT fibers that were extruded from CNT/acid solutions; most likely the conductivity enhancement is due to acid doping. Liu et al. [24] reported 1.08x10⁻⁵ Ω*m for as produced MW-CNT fibers. Zhong et al. [17] reported resistivity of 2x10⁻⁶ Ω*m [17] for as-spun MW-CNTs. The lowest resistivity reported to our knowledge was achieved by Zhao et al. [1] through chemically doping CNTs with iodine, 5x10⁻⁷ Ω*m [9].

During these experiments, variation in the diameter of the CNT fibers, near the contact point with the electrode, were observed. Additionally, different accumulations of Ag paste near the contacts are seen, most likely due to the wetting of the CNT fiber by the solvent in the Ag paste. SEM images of the CNT yarn and electrode contacts reveal that the silver paste diffuses along the CNT fiber surface near the metal contact interface. Also, small diameter reductions in the CNT diameter were observed near the applied Ag-paste. Our conclusion is that the small variations on the Au doped conductivity measurements are the result diameter changes and deformation of the fibers as a result of densifications and wetting. During the course of our experiments we have observed that the relative electrical resistance between samples seems a quite reliable measurement more than the absolute electrical resistance and resistivity measurement, because smaller discrepancies between samples from the same fiber have been observed in resistance measurements compared to resistivity measurements.

Figure 4. SEM images of: (a) Au doped CNT fiber showing some Au nanoparticle formation at doping; (b) electrical resistivity of pristine and Au doped CNT fibers compared to Au and Cu wires. Additional resistivity reports from the literature are represented by Davis et al [5], Zhao et al [1], Behabtu et al [17], Liu et al [24] and Zhong et al [17].

Insulating coatings on CNT fibers are required before they can be used in electrical devices, similar to the way that metal wires are insulated in order to be used as electrical conducting cables. Among the different polymers that are currently being explored at the Nanoworld Labs for this purpose, hydrogenated nitrile butadiene rubber (HNBR) seems the most promising candidate. HNBR, besides the uniformity of its coating, has additional advantages, such as flexibility, elasticity, and resistance to oil and water. The polymer coating is performed by a simple dip-coating approach. We submerge the CNT fiber into the polymer solution and pull the end out of the solution at a constant speed onto a collecting bobbin. The collecting bobbin pulls the thread, as it rotates on its own axis, which is a shaft of an electrical DC.
motor; this motor allows rotation-speed control of the pulling bobbin. Furthermore, the speed of the collecting bobbin allows applying tension, while the thread is pulled after coating. Normally, the pulling speed is in the range of ~9 rpm; this is varied, depending on the CNT fiber diameter. Thinner fibers need slower speeds to prevent them from breaking. A simple remedy to avoid CNT fiber breaking is to increase the thickness, or to increase the number of plies that CNT fiber is made of. Increasing the diameter requires wider, uniformly spinable CNT arrays, in order to keep diameter consistent. The alternative, increasing the number of plies, seems a better option; however, making plies requires a careful and even-twist on each conforming ply. Small twisting mismatches generate localized stresses in sections of the CNT fiber, which tend to form twists and loops after polymer coating. As a result, the polymer coating tears and leaves the exposed CNT fiber. Due to these experiences, our results are based on single ply CNT fibers between 15 and 30 um in diameter, and tens of meters in length, that can be manipulated and processed without breaking.

Another intent of polymer coating the CNT fiber is to encapsulate the dopant ions and molecules within the CNT fiber. As reported in literature, exohedral doping has shown improvements of the electrical conductivity of CNTs in mats and buckypaper, and recently in fibers[9]; however, over time some of the dopants have shown a decay in performance. It has been suggested that a resistivity increase of CNT fiber would be the result of dopant ions or molecules leaving the CNT surface. Among the most common dopants are HNO$_3$, hydrazine, and Au. Particularly in the case of HNO$_3$ and hydrazine, the dopant concentration appears to decrease with time. As a result, the electrical resistivity of the CNTs fibers increases, nearing the electrical resistivity of the untreated material. A polymer coating is expected to encapsulate the dopants in the CNT fibers, thereby avoiding dopant leeching into the atmosphere, and maintaining the improved electrical conductivity.

4. Conclusion

Insulated and electrically conducting Au doped CNT fibers were successfully produced. The CNT fiber was spun from VA-CNT arrays, chemically doped to increase electrical conductivity, and coated with a flexible polymer for protection and insulation. Chemical doping using Au dissolved into solution, decreased the fiber’s electrical resistivity by one order of magnitude. The polymer coating was performed using a common industrial polymer, HNBR that is flexible, oil resistant and electrically non-conducting. The microcable produced could eventually be used in the fabrication of coils for electrical motors and lightweight electromagnetic devices.

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