Transforming pristine nano-materials into practical macro-materials: a look at novel thermal processing methods for CNT fibers

1. Abstract

Carbon nanotubes (CNTs) have many desirable properties, such as strength that outperforms steel by weight [1], electrical conductivity that outperforms copper [2, 3, 4], as well as interesting optical, semi-conducting, and other properties [5]. However, these characteristics have not been realized at a meaningful scale. Carbon nanotube fiber (CNTF), fiber spun in a variety of ways from CNTs, has elevated the importance of carbon nanotubes and given their anisotropic properties relevance [6]. This fiber has the potential to exhibit, in some fraction of magnitude, the same properties as its constituent CNTs, as well as have a diversity of significant practical uses [7, 8, 9]. This will require, though, more controlled production and novel post-production processing methods. Herein, we will investigate emerging thermal processing techniques and briefly cover their mechanisms.

2. Background

The world was once promised a space elevator made entirely of carbon nanotubes [10]; this is not possible now and may never be possible, but carbon nanotube fibers bring the world closer to accessing the extraordinary capabilities of CNTs. CNTs have ideal mechanical electrical, and thermal properties [8, 7]. These properties cannot be realized at a practical scale because methods for growing these 'perfect' carbon nanotubes have not reached a level where they can be produced at a length that is useful structurally or mechanically. Aside from electronics, a field whose needs may be addressed by the as-grown length of CNTs [9, 11], CNTs predominantly serve as a component in a larger system, rather than as a useful product in and of themselves [12].

Some of the central roles carbon nanotubes play in materials today are as constituents of a mixture, such as alloys in metals, additives in polymers, and in coatings. Early adopters of CNTs saw use in enhancing the electrical properties of plastics, using CNTs as fillers that form a conductive network within the plastic and allow for electrostatic-discharge [13]. Moreover, carbon nanotubes, even at small loading, can impart greater toughness and stiffness to plastics, without altering much the advantageous properties of the plastic itself [14]. The mixture of CNTs in cement, to improve both compressive strength and conductivity, also shows promise [15].

Additionally, several techniques have been developed that produce fibers composed of CNTs of substantial length. These techniques are generally broken down into two main types - wet-spinning methods and dry-spinning methods - and will be explained briefly [6]. The wet-spinning method involves dispersing prefabricated CNTs in solution; then using industry standard processing methods, the continuous fiber is extruded and coagulated into its final state [16]. Of the two dry-spinning methods, the technique discovered first involves drawing CNT fiber from a forest of Chemical Vapor Deposition (CVD) grown CNTs [17]. The other common dry-spinning method incorporates spinning the fiber while it is being grown in a CVD furnace, this method has been coined the 'Floating Catalyst Method' [17].

Neither wet nor dry-spinning generate flawless carbon nanotube fibers. These methods have, however, reached a level of proficiency where fibers produced under the same conditions are comparable, or have similar hallmarks. Among the production methods, end-product fibers do not usually resemble one another. This is because the constituent carbon nanotubes are, for the most part, drastically different. The variety of mutually exclusive carbon nanotube properties, principally influenced by the chirality, the number of walls, and CNT length will not be discussed in this review. The properties of a fiber will be affected by the properties of its component CNTs, as well as the CNT loading for a fiber that is composed only in part by CNTs (composites) among other factors.

As spun, or unprocessed, solid-state spun single wall carbon nanotube (SWCNT) fibers can have exceptionally high electrical conductivities, they however, lack the tensile strength of their wet spun counterparts [18]. Defects in the component CNTs as well as poor interfacial contact between the CNTs composing the fiber explain this poor mechanical behavior [18]. Some dry processing methods aim to improve the properties of these CNT fibers by targeting the issue of interfacial contact. Densification by twisting, loading, and thermal treatments are currently being researched to address the poor mechanical properties of these fibers [18]. Additionally, some of these methods also allow the recovery of defects in the CNTs and the junctions in between CNTs [19]. It is the goal of this review to evaluate and compare novel processing methods, not production methods. For this reason, we will address novel dry processing techniques, specifically thermal techniques, as they apply to dry-spun CNT Fibers.

3. Thermal Processing of Carbon Nanotubes

Annealing heat treatments have shown promise for recovery of defects in carbon nanotubes, specifically with regard to 'cleaning' the nanotube bundles of metal catalysts and amorphous carbon [19]; because of this, many groups researching post-processing methods for

CNT fibers have sought to apply the same methodology for as-spun CNT fibers. In addition, but related to cleaning, Chen et al. have shown structural enhancements can occur in the range of 1800-2200 °C, for disordered MWCNTs. As CNTs are exposed to temperatures in the 1800 °C range, the CNTs first become more disordered: the outer edges of the structure become undulated as a result of the evaporation of metal catalysts and amorphous carbon, which leaves voids in the structure. As thermal annealing continues, 2000 °C, the voids in the center of the CNT bundles are reduced, however the sides still show significant disorder in their wavy appearance. Nearer 2600 °C, the tubes show bulk graphitization and walls that have far less undulation. The authors note that at these temperatures, and higher annealing temperatures, some 'gross defects' will always remain due to limited release of strain energy in these structures.

Research has also shown that thermally treating CNT fibers can enhance their properties [18, 20, 21]. *The thermal treatment phenomenon that applies to CNTs does not directly apply to CNT assemblies or fibers.* Because these fibers are composed of large bundles - which in turn are composed of small bundles of carbon nanotubes - the mechanisms governing the dynamics of cleaning and defect recovery will have more complicated affects in CNT fibers than CNTs alone. We will address research on several heat treatment methods conducted on CNT fibers: conventional/furnace annealing, laser heat treatment, and current-induced thermal treatment.

3.1. **Conventional/Furnace Annealing.** In a paper by Li et al., seeking to produce high conductivity fibers and investigate the conduction mechanism of CNT fibers, several processing methods were undertaken. Two of these methods are within the scope of this review [18]:

- Annealing in air at 480 °C - to clean amorphous carbon
- Annealing in Ar + 6% H2 at 800 °C - to saturate defective structures

CNT fibers do not show the properties of their constituent CNTs because of poor interfacial contact. In the case of the current study, semi-conductive multiwalled carbon nanotube fibers show lower than expected conductivity because of electrical contact resistance at CNT-CNT interfaces.

It is shown that resistance decreases when the fiber is annealed with Hydrogen and increases when annealed in air at only 480 °C. Li et al. also conducted structural analysis with Raman spectroscopy. The lower I_G/I_D ratio of the fibers found after thermal treatment indicates that the fibers became more disordered. The I_G/I_D ratio refers to the ratio of intensities of the G and D vibrational band, a common metric for measuring crystal defectiveness in graphene; the lower this ratio the more defective the crystal. Although these processing methods appear to introduce defects while changing the conductivity, they offer an exciting method for tailoring the electronic properties, as needed for a desired application.

These results appear to conflict with previous research of thermal treatment creating more ordered CNTs [19]. However, the goals of Li et al. were not to improve the mechanical properties of the CNT fiber. Additionally, the aforementioned structural enhancement induced by annealing temperatures between 1800-2200 °C, use temperatures far greater than Li et al. and as such the same mechanisms do not apply. It may also be relevant that annealing at such high temperatures requires ultra-high-temperature (UHT) furnace, unless alternative treatment methods are used: like the following laser sweeping treatment or current induced heat treatment. Use of a UHT furnace may not be economically practical for research or potential consumer purposes.

3.2. **Laser Sweeping Heat Treatment.** In"Fabrication and processing of high-strength densely packed carbon nanotube yarns without solution processes", Liu et al. develop an innovative device for producing CNT fiber and employ a novel method for post production treatment of the fiber [18]. The goal of their study was to enhance the multifunctional properties, i.e. mechanical strength and electrical conductivity, of CNT fiber. The laser sweeping treatment used by Liu et al. shows potential for enhancing the properties of the fiber through recovering defects in the CNTs as well as welding CNT joints, improving interfacial contact.

The setup for the laser sweeping treatment includes a computer controlled CO_2 laser at 30 W and a vacuum chamber with a germanium window at $\sim 10^{-6}$ mbar. The laser is passed from one end to the other end of the fiber, with a sweep speed that ranges from 10 to 50 mm/s. Liu et al. reason that, because CNTs absorb light well, the laser treatment will result in a relatively uniform heat distribution, so as not to create any concentrated points of heat. Or, more directly: this may avoid issues related to the fiber developing internal stresses due to uneven thermal strain.

The laser sweeping treatment results in fibers with drastically greater Young's Modulus, E, and conductivity. The data shows that at sweeping rate of 50 mm/s the tensile strength increases by 12% and with sweeping rate $>$ 50 mm/s the tensile strength decreases. Although not specifically mentioned, we attribute this to the phenomenon discussed earlier, where around 1800 °C the fiber shows more structural disorder due to internal voids, then with increasing temperature 2000 -> 2600 °C the fiber becomes more ordered. This hypothesis is further supported with Raman spectroscopy data, where the I_G/I_D ratio increases with slower sweep rate. All in all this technique of sweeping laser thermal treatment shows great promise. Additionally, it offers the advantage that the method could be easily incorporated into current fiber manufacturing methods so that it might be a part of a continuous process.

3.3. **Current Induced Heat Treatment.** Current induced heat treatment also offers several advantages, and is scalable [20]. Zhang et al. appended it to their novel spinning process and achieved a stiffer, i.e. higher E, however lower tensile strength CNT fiber. This change in mechanical properties after heat treatment is remarkably similar to the results achieved by Liu et al. above.

For their study, Zhang et al. passed a high current through the fiber for several hours, with a current induced temperature rise caused by joule heating, bringing fiber temperature up to 2000 °C. It is notable that this temperature is in the structure change regime mentioned earlier [19], which explains the change in mechanical properties. Zhang et al. account for the decrease in tensile strength by citing that joule heating causes areas of the fiber with defects to reach much higher temperatures than the average, meaning that some point defects likely had temperatures far exceeding 2000 °C. It may also be the case that the temperature in some areas were not high enough to fully relieve the internal stresses caused by catalyst cleaning and fiber welding [19]. If this is true, then any voids remaining in the fiber might have served as points for stress accumulation, which might lower the overall tensile strength of the fiber.

It was shown in a previous study that anneal time does not have a very significant impact on structure change, however magnitude of temperature does [19]. So it is likely that the several hour current induced heat treatment was unnecessarily long. However, Zhang et al. showed an interesting application of heat treatment that may have depended on treatment time. Specifically, the study shows a memory effect after heat treatment. This enabled the group to create a spring that retained its shape after heat treatment.

4. Conclusion

CNT fibers serve as the initial realization of the fantastic unidirectional properties of carbon nanotubes. However, CNT Fibers fall far short of the bar set by the performance of pure CNTS. Novel processing techniques have recently emerged that show enticing results, which suggest that this lackluster performance may soon change. Heat treatments, in particular, show great promise because they are relatively easy to implement. It is integral that we continue optimizing and improving these methods - as well as resolving how constituent CNT structure affects and is affected by these treatments, which was not addressed in this review.

For economic uptake, it is almost just as important that these methods also be scalable or even better - easily joined with existing manufacturing methods. The thermal processing methods discussed in this review are some examples of techniques that fit these criteria - especially laser sweeping heat treatment [18] and current induced heat treatment [20]. These procedures have been shown to improve mechanical properties, electrical properties or both.

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