Chapter 7
CNT Applications in Specialized Materials

Contents

7.1 Overview

As noted in an earlier chapter, *specialized materials* include those possessing high strength, high conductivity (electrical as well as thermal), greater elasticity, high electromagnetic absorption (e.g., for radar cross-section (RCS) reduction), and other desirable properties. The high-strength applications encompass not only postulated esoteric applications such as “elevators to space” [141] but also more mundane ones (and ones that have actually found some commercial application) such as yarns for more durable textiles and composite materials with higher strength and greater durability. It is also to be noted that although SWCNTs show greater promise for CNT-based specialized materials in theoretical and limited, laboratory, experimental studies, most efforts at developing practical products have concentrated on MWCNTs, due to their considerably lower cost and greater ease of fabrication in bulk quantities.

7.2 Textiles

A first requirement for potential use in *textiles* is to successfully spin CNTs into *yarns* with improved bulk properties (such as tensile strength, elasticity, modulus, etc.) as compared to conventional yarns, even if these properties do not approach those for individual or a few CNTs. Such fabrication methods have included in situ chemical vapor deposition (CVD) spinning to produce continuous CNT yarns from CVD-grown CNT aerogels or drawing out CNT bundles from CNT forests and

P. Chandrasekhar, *Conducting Polymers, Fundamentals and Applications*,
https://doi.org/10.1007/978-3-319-69378-1_7

subsequently twisting them into fibers using the “draw-twist” method [142, 143], or “co-spinning” with other fibers, such as cellulose-based fibers and other methods [144–149]; however, these processes usually yield very high strengths or other desirable properties only for short (about 1 mm) pieces of yarn, but strengths that are 1/10 or less of these for yarns are longer than 10 mm. In rare instances, SWCNTs with lengths up to several cm have been fabricated (in that case via catalytic pyrolysis of n-hexane) [150]. Spinning of MWCNTs produced in CNT “forests” has been used to produce two-ply yarns with the appearance of cotton or wool, a density of about 0.8 g/cm^3, and a tensile strength of 460 MPa [151, 152].

A process for pressure-induced interlinking of CNTs has been proposed for weaving them into high-strength *fibers* and, ultimately, high-strength cloth for applications such as bulletproof cloth [153]; once again, however, the practical (let alone commercial) implementation of this novel application is lacking to date. Applications sought have included textiles that have antibacterial, flame retardant, electrically conductive (e.g., for electromagnetic impulse (EMI) shielding), and other very wide-ranging properties [147–149].

Data have been published showing that yarns made from high-quality MWCNTs have reached a stiffness of 357 GPa and a strength of 8.8 GPa but only for a gauge length that is comparable to the mm-dimension CNTs within the yarn. On the other hand, cm-dimension gauge lengths displayed a strength of 2 GPa, corresponding to a gravimetric strength equaling that of commercially available Kevlar (DuPont). It has been noted that macroscale CNT yarns never achieve theoretically predicted strengths primarily because the probability of critical flaws increases with scale [18, 46, 154]. A process for the production of high-performance fibers containing *aligned* SWCNTs using coagulation spinning of CNT suspensions has been demonstrated in the laboratory [155], but scale-up of this process has not been demonstrated to date.

7.3 Composite Materials

Due to the high cost of producing SWCNTs, or MWCNTs with a specific diameter range and chirality, CNTs used in composite materials have, to date, primarily comprised bulk (bundles of) CNTs. Nevertheless, incremental improvements in mechanical, thermal, and electrical performance parameters have indeed been achieved in such materials. Examples of applications of this nature *currently implemented commercially* include:

- Use in bicycle components such as handlebars and seat bases for greater strength and in marine products, including small boats, implemented by Zyvex Technologies [140].
- The *Hybtonite* brand of carbon–epoxy composites manufactured by a Finnish company, Amroy Europe Oy [2058], wherein conventional carbon fiber is replaced by CNTs, yielding materials with up to 30% greater strength than

standard graphite–epoxy composites. Claimed applications for these composites are as varied as ice hockey sticks, surfboards, skis, and wind turbines.

Regarding mechanical properties of composite materials, it has been observed that the major difference of CNTs from conventional, fiber-reinforced composites is that the scale is narrowed to nm from μm and that CNTs can impart high stiffness as well as high strength [156, 157]. For example, it has been claimed in one study that, for load-bearing applications, CNT powders mixed with polymers or precursor resins can increase stiffness, strength, and toughness, and adding ca. 1 w/w% MWCNTs to epoxy resin enhances stiffness and fracture toughness by 6 and 23%, respectively, without compromising other mechanical properties [18, 158, 159]. However, it has not been clear from these studies whether these properties are improved enough from those of corresponding composites containing graphite or other carbon forms to warrant the extra cost involved in fabricating CNT-containing composites.

One of the critical issues in obtaining high-performance CNT-based composite materials is the achievement of good adhesion between the matrix and the individual CNTs, required for an effective transfer of the mechanical load onto the CNTs [19]. One approach to achieve this is polymer synthesis from covalently attached initiator sites, e.g., in radical polymerization of methacrylate esters on CNTs [160].

In other recent work, CNT-containing fiber composites have been created by growing aligned CNT forests onto glass, SiC, alumina, and carbon fibers. Fabric made from CNT-SiC impregnated with epoxy displayed in-plane shear interlaminar (mode II) toughness by 54%, and similar CNT-alumina fabric showed 69% improved mode II toughness (41). Applications proposed for such have included lightning strike protection and deicing for aircraft [18, 158, 161, 162], although, again, to date no commercial products have yet emerged.

Silica-coated MWCNTs have been prepared using sol-gel techniques combined with thermal annealing, which are claimed to be resistant to combustive oxidation up to about 1200 °C [163].

Aluminum-MWCNT composites with strengths comparable to stainless steel (0.7–1 GPa) at one-third the density have been demonstrated [18]. Again, however, to date no commercial product has emerged from this work.

MWCNTs have also been proposed as flame retardant additives to plastics (to replace halogenated flame retardants which have environmental issues), emanating from rheological changes induced by CNTs loading [164].

It has also been observed that, by replacing the carbon black in rubber tires with CNTs, improved skid resistance and reduced abrasion are obtained [165]; (needless to say, in spite of all these excellent experimental results, as of this writing, there are no automobile tires on the market that incorporate CNTs.) In other elastomeric applications, a CNT–[amine-terminated poly(dimethylsiloxane) (PDMS)] composite was developed with tensile modulus, and elongation at break vastly improved over corresponding PDMS control materials [166].

With respect to electrical conduction properties (e.g., when CNTs are added into resin precursors of composites to increase their electrical conductivity), CNTs' high aspect ratio is said to allow them to form a percolation network at low concentrations (<0.1 w/w%); in some cases, polymer composites fabricated with MWCNTs at a 10 w/w% loading have claimed conductivities of 10,000 S/m or higher [18, 167]. Quite logically, highly electrically conductive CNT composites have been proposed for use in electromagnetic interference (EMI) shielding and electrostatic discharge (ESD) prevention, e.g., as packaging for microelectronics and in spacecraft (NASA's Juno spacecraft apparently used a partial CNT-based shield for ESD prevention) [18].

Other, varied applications of CNTs have included scaffolding for bone cell growth [168] and coatings for radar cross-section (RCS) reduction, where the high absorption of MWCNTs in the microwave region combined with their "blackness" in the UV-Vis-NIR and IR spectral regions is an advantage. To date, however, practical implementation has not been possible due to immunological and toxicological issues in the former application and inability to compete with standard RCS coatings such as the conducting polymer poy(aniline) (due to cost and related issues) in the latter application [169].

7.4 Problems and Exercises

1. Briefly describe typical methods used to incorporate CNTs in textiles. Name at least two proposed applications.
2. Name at least one product type in the category of composite materials where CNTs have been commercialized as of 2016.
3. What are the advantages and drawbacks of the use of *coated* MWCNTs in composite materials vs. uncoated MWCNTs? Support your answer from the physical principles behind the strength of composite materials.