Chapter 1

Introduction

1.1 Goals and contributions

The main goals of this dissertation are (i) the characterization of the dynamic response of macroscale, aligned carbon nanotube foams, (ii) the study of the effects of microstructural features on the bulk functional properties and on the fundamental deformation mechanisms of these materials.

Aligned carbon nanotube (CNT) foams derive their unique mechanical properties from the hierarchical organization of structural features across different lengthscales, ranging from nanometers (e.g., the structure of single tubes) to millimeters (e.g., the ensemble of many intertwined tubes). Due to their complex morphology and their high deformability, they exhibit intriguing deformation responses at different loading regimes. Understanding these fundamental deformation mechanisms and the material responses at high rate deformations are crucial to the identification of critical design parameters for new, lightweight materials for energy absorption and impact protection applications. Furthermore, aligned CNT foams can serve as a model material for the study of the mechanical response and the structure-function relations of other hierarchical materials with fibrous morphologies.

Over the last few years, the macroscale aligned carbon nanotube foams have been studied extensively in the quasistatic strain rate regime. It has been shown that they exhibit a stress-strain response that is similar to other foam materials, have the ability to dissipate energy through hysteresis, and present strain localization and characteristic sequential buckling during compression. However, their response in high strain rate regime that is relevant to the protective applications for which the CNT foams are proposed, is not fully characterized. Further, the effects of their nano- and micro-structures on the bulk dynamic response of CNT foams also remain elusive. This dissertation presents the fabrication, characterization and numerical modeling of such aligned CNT foams with different controlled nano- and micro-structures to provide understanding of the key structure-function relations of these fibrous, hierarchical materials and their rate-sensitive mechanical properties.

The key contributions of the work described in this dissertation are:

1. The development of a new experimental testing platform to measure and observe the dynamic responses of complex, soft materials *in-situ*.
2. The fabrication of macroscale carbon nanotube materials with varying, controlled microstructures, through chemical vapor deposition synthesis techniques and photolithographic approaches.
3. The characterization of the morphology and structure of the carbon nanotube foams using experimental techniques such as scanning electron microscopy, transmission electron microscopy, and synchrotron x-ray scattering and mass attenuation measurements.
4. The characterization of the mechanical response of the carbon nanotube foams in the medium- to high-strain-rate regime.
5. The identification of the key structure-property relations linking relevant constituent features at different lengthscales with bulk functional properties of the materials.
6. The development of numerical models to describe the dynamic response of aligned carbon nanotube foams.

At a fundamental level, this study contributes to improve our current understanding of the contribution of nano- and micro-structures to the bulk dynamic behavior of hierarchical materials with fibrous morphology. This study also characterizes the mechanical performance and energy dissipative characteristics of CNT foams using different figures of merit, such as elastic modulus, transmitted peak stress, compressibility (maximum strain), hysteretic energy dissipation, cushion factor and specific energy absorption (energy absorption per unit mass). It should be noted that the mechanical properties reported in this dissertation are effective properties of the macroscale CNT foams. They were obtained by treating CNT foams as bulk materials, even though there are structural features present across several lengthscales along the hierarchy. Therefore, the bulk response can be perceived as material response of the CNT foams, although the bulk response is strongly influenced by the structural response of different features present across the different lengthscales from nano- to micro-scales. Fully understanding the mechanical response of hierarchical CNT foams will guide the design of novel lightweight materials with superior mechanical properties and energy absorption capabilities.

1.2 Organization and a brief overview of the dissertation

The remainder of Chapter 1 describes the broader context in which this research is set, and provides an introduction to carbon nanotubes (CNTs) and CNT-based materials and their relevant applications.

Chapter 2 provides detailed information on the experimental techniques used. It describes floating-catalyst and fixed-catalyst thermal chemical vapor deposition (tCVD) synthesis techniques for the fabrication of the vertically aligned carbon nanotube (VACNT) arrays, and the characterization techniques used to analyze the microstructure of CNT foams (e.g., synchrotron x-ray scattering, and mass attenuation measurements and electron microscopy). It also details the quasi-static mechanical testing setup and the dynamic characterization techniques developed as part of this thesis to characterize soft, complex materials.

Chapter 3 describes the VACNT foams' microstructures, morphologies, and their intrinsic density gradient. It then presents and discusses the experimental results obtained testing VACNT foams under impact. The discussion correlates VACNT microstructure and material density to bulk dynamic properties. The effect of deformation rates on the VACNT bulk mechanical response is also presented. Finally, the chapter describes the contribution of the fundamental structural features found at different length scales to the deformation mechanisms and energy dissipative characteristics of bulk foams.

Chapter 4 presents the characterization and mechanical response of helically coiled carbon nanotube (HCNT) foams—hierarchical foams made of CNTs with helical geometry. The morphology of the HCNT foams characterized by scanning electron microscopy and transmission electron microscopy are presented first, and then the HCNT fiber alignment characteristics and the intrinsic density gradients characterized by the synchrotron x-ray scattering and mass attenuation are presented. Subsequently, the mechanical response of HCNT foams in quasistatic and dynamic loading regimes are discussed and their responses are correlated to the measured morphology and intrinsic functional property gradients. Their mechanical response is also compared to the VACNT foams' response, to clarify the effect of their microstructural differences.

Chapter 5 discusses the design, synthesis, and dynamic response of VACNT foams with patterned micro-structural features. The chapter presents in detail the fabrication process used, which combines photolithographic techniques with the CVD synthesis process. The effects of different geometrical micro-patterns on the bulk mechanical responses and the fundamental deformation mechanisms of the foams are examined.

Chapter 6 presents the synthesis and the dynamic response of the VACNT foams with microscale heterogeneities. The microscale heterogeneities were engineered through synthesizing alternating 'soft' and 'stiff' intermediate CNT bands. The dynamic response of these VACNT foams is compared to their quasistatic response. The influence of the heterogeneous bands on the deformation mechanisms and its application to impact protection are discussed.

Chapter 7 presents a numerical model based on bi-stable springs and point masses that describes the dynamic compression of the VACNT foams. The application of this model to two VACNT samples impacted at two different velocities and the mechanical parameter identification in length scales that are smaller than the height of those samples are discussed.

Chapter 8 concludes the dissertation and provides an outlook on the future works.

Two appendixes follow Chapter 8. Appendix A presents the quasistatic mechanical response of VACNT foams synthesized using the fixed-catalyst CVD process. A unique buckle characteristic—buckles with much smaller wavelengths inside the sample compared to the buckles observed on the external surface of the VACNT foams—is discussed in detail and the findings are supported by a simplified Euler buckling analysis.

Appendix B presents the wave propagation characteristics in a periodic array of VACNT foams alternated with rigid interlayers. Here, we demonstrate a unique wave propagation characteristic, where the effective wave velocity decreases with the increasing impact force exhibiting a softening response. We develop an analytical model with rate-independent hysteresis for the VACNT foams. We use this dissipative spring element in a numerical model of a chain of masses and springs to support and explain the underlying physics of the wave slow-down response observed in experiments.

1.3 Introduction

In much the same way that our mastery of silicon processing has led to the modern era of information technology, developments in advanced materials are expected to fuel emerging technologies that address some of the most pressing challenges of our time; from issues of clean energy to problems in national security and human welfare [1]. Materials that optimally combine stiffness, strength and toughness are critical for many engineering applications—protecting humans and engineering systems from impact and vibrations, building durable electronics, and creating efficient energy storage materials, bio-compatible prostheses and artificial organs, to name only a few. Recently, advanced materials with engineered microstructures have been developed, which realize several functional properties in unprecedented ways. For example, micro- and nano-structured metamaterials with deliberate internal structuring have been shown to exhibit extraordinary properties such as the presence of tunable phononic band gaps, superior thermoelectric properties, high specific energy absorption, and other properties that do not commonly exists in conventional materials like negative Poison’s ratio, negative dynamic modulus and negative effective density [2]. Similarly, synthetic hierarchical materials synthesized by taking inspiration from the design principles found in nature, can achieve property amplification in a non-additive manner, surpassing the simple composite rule of mixture formulations [3]. These recent developments have led to an increasing interest in understanding material behaviors at multiple length and time scales.

Over the last two decades, carbon nanotube (CNT) structures have been created in a variety of length scales, from individual nanoscale CNTs to foam-like materials and structures at the macroscale. The CNTs and the CNT-based materials have been shown to exhibit novel electrical, thermal and mechanical properties, leading to a rapidly advancing development of a next generation of materials and material systems. In addition to the many potential applications proposed, the hierarchical microstructure of macro-scale CNT-based materials and the ability to considerably control their microstructure by varying synthesis techniques make them an excellent model candidate for carrying out fundamental studies on the mechanical behavior of other complex materials.

1.4 Carbon nanotubes

Carbon nanotubes (CNTs) are an allotrope of carbon that belongs to the fullerene structural family. ‘Fullerene’ identifies the family of molecules that are entirely composed of carbon and have a hollow structure in spherical, ellipsoidal and cylindrical shapes (e.g.: buckminsterfullerenes or bucky balls (C_{60}), carbon nanotubes, fullerene rings). CNTs are often thought of as a rolled-up graphene sheets that are entirely made of sp^2-bonded carbon atoms [4], though they are synthesized differently, as discussed in the following sections. Though CNTs got broad attention after their discovery, reported by Iijima et.al. in 1991 [5], their origin dates back to the 1950s (see [6,7]). Their properties significantly depend on the direction in which the graphene sheets are rolled into cylinders, referred to as the chirality or the helicity of the CNT. The chiral vector and the chiral angle define the chirality of the CNT, describing various types of nanotubes including zig-zag, armchair and chiral versions (see the articles by Dresselhaus et.al. [4,8], for extensive details). Depending on their chirality, CNTs can be electrically conductive or semiconductive [9] and exhibit very different mechanical properties in their Young’s modulus, Poisson’s ratio and critical buckling strength [10,11]. These effects of chirality are strongly pronounced for smaller diameter tubes, and become unimportant as the diameter gets larger [10,11].

Depending on the number of walls present, CNTs are classified into single-walled CNTs (SWCNTs), double-walled CNTs (DWCNTs), and multi-walled CNTs (MWCNTs). MWCNTs form concentric cylinders with an inter-wall spacing, typically of around 0.34

nm [4,12]. Even though 0.34 nm is the interlayer spacing between two graphene layers, the wall spacing can be up to 10% higher depending on the number of walls present in the MWCNT and the diameter of the MWCNT, with the later having a more pronounced effect [12]. The increase in inter-wall spacing with decreasing diameter is attributed to the increased repulsive forces that arises from large curvature [13]. The strain energy of a CNT is proportional to $1/R^2$, where R is the radius of the CNT [14]. The CNTs with larger inter-wall spacing resulting from higher strain energy are more reactive because of their reduced stability [13]. The weak interaction strength between the outermost wall and the neighboring inner wall of highly pure MWCNTs has been measured through inter-wall shearing and found to be between 0.08-0.3 MPa [15]. However, MWCNTs often have defect-related bridging from wall to wall, for example through an sp^3 covalent bond, and therefore exhibit higher inter-wall shear strength.

Several properties of individual CNTs have been measured experimentally and they have been shown to exhibit extraordinary electrical, thermal and mechanical properties [8]. They can be electrically superconductive [16], exhibit thermal conductivity over 3000 $Wm^{-1}K^{-1}$ (10 times higher than copper) [17], withstand current densities of up to 10^{10} A/cm^2 (1000 times higher than copper) [18], and have Young's moduli of 0.4-4.15 TPa [19]. Due to their low density, they exhibit excellent specific properties: for example, CNTs can be ~100 times stronger than steel while having weighing only a sixth as much [20]. They also have been shown to be stable at up to 3400 K in vacuum [21] and 2073 K in argon [22]. Even though CNTs exhibit exceptional properties as individual fibers that can directly benefit applications in nano-electronics and nano- and micro-electromechanical systems (NEMS and MEMS), tapping into their exceptional properties for macroscale engineering systems remains challenging [23], although there has been some recent progress in this regard [24].

The remainder of this dissertation focuses on these bulk properties of the CNT structures and their relationship to the organization of the CNT fibers across different length scales. Further, the discussions hereafter are limited primarily to the mechanical properties of CNT structures and their fundamental deformation mechanisms at different length scales.

1.5 Synthesis of carbon nanotubes

There are numerous synthesis techniques for fabricating CNTs, such as arc discharge, laser ablation and thermal chemical vapor deposition (tCVD), and liquid plasma enhanced chemical vapor deposition (PECVD). Among these, tCVD is the most popular method due to its ability to synthesize large quantities of CNTs with relative ease and its feasibility of transitioning to industrial-scale mass production [24,25]. Metal catalysts, such as Fe, Co and Ni, that are known to catalyze graphitic carbon in tCVD systems [26] are either deposited as a thin film on the substrate prior to synthesis or deposited during synthesis in vapor phase. The former technique is called the ‘fixed-catalyst’ or ‘pre-deposited catalyst’ method, and the latter is referred to as the ‘floating-catalyst’ or ‘continuous-catalyst’ method. In the fixed-catalyst method, the deposited thin film catalyst is broken down into nanoparticles, first using pre-treatment with gas (e.g. hydrogen annealing) and/or temperature [27,28]. In contrast, the floating-catalyst method uses metallocenes as metal precursors, which then decompose at temperatures of less than 500 ^{o}C to free the metal atoms [29]. In the presence of a catalyst, a hydrocarbon source is broken down into simpler carbon compounds, metastable carbides are formed, and finally, the rapid diffusion of carbon into the catalyst’s interior leads to precipitation of graphitic carbon in tubular form [26]. The fixed-catalyst system results in reasonably purer CNTs with controlled morphologies, whereas the floating catalyst system results in reduced purity [23]. However, the floating-catalyst process is advantageous for scaling towards large-scale production. When synthesizing macroscale arrays of CNTs using these two CVD techniques, fixed-catalyst synthesis results in small diameter CNTs (5-15 nm) with few walls (including synthesis of SWCNTs) whereas the floating-catalyst synthesis results in large diameter CNTs (20-80 nm) with several walls [23]. This also affects the porosity, where the fixed-catalyst samples have a porosity of 95 - 99% with ~0.05 g cm^{-3} density while the floating-catalyst samples have a 80 – 90% porosity with densities ~ 0.3 g cm^{-3} [23].

In both methods, several synthesis parameters such as substrate, catalyst size distribution, gas composition, gas flow-rate, feedstock input rate, temperature, and pressure influence the resultant CNT morphology and properties, presenting a number of tuning-parameters which can be used to change the structure of the CNTs and resultant properties. For a comprehensive review of synthesis methods and the effects of the synthesis parameters on resultant CNT structures, see the doctoral dissertation of Jordan R. Raney (Caltech) [23]. Floating-catalyst and fixed-catalyst CVD synthesis techniques specific to this research are discussed in Chapter 2.

1.6 Bulk carbon nanotube structures and their mechanical properties

Recently, several 1-D, 2-D and 3-D macroscale structures have been fabricated from CNTs. This section discusses some of the significant advancements made regarding these CNT macrostructures and their mechanical properties.

One-dimensional fibers spun from individual CNTs to lengths up to 20 mm have shown a superior tensile strength of up to 8.8 GPa and a tensile modulus of 357 GPa [30]. Their specific strength and specific stiffness are much higher than current commercially available carbon and polymer fibers [30]. However, variations have been observed in different studies due to differences in the primary CNT structure and the geometry of the fabricated fiber, yielding a broad range of tensile strengths (30-357 GPa) and tensile moduli (0.2-8.8 GPa) reported in the literature [31].

Similarly two-dimensional thin sheets drawn from MWCNTs and densified into identically-oriented or orthogonally-oriented layers have been shown to exhibit specific strengths of 465 GPa $(\mathrm{g\ cm^{-3}})^{-1}$ and 175 GPa $(\mathrm{g\ cm^{-3}})^{-1}$, respectively [32]. These specific strengths are significantly higher than or comparable to ultra-high strength steel (125 GPa $(\mathrm{g\ cm^{-3}})^{-1}$), aluminum alloy sheets (250 GPa $(\mathrm{g\ cm^{-3}})^{-1}$) and the Mylar and Kapton films (160 GPa $(\mathrm{g\ cm^{-3}})^{-1}$) used in ultra-light air vehicles [32]. Thin film bucky-papers made of randomly oriented CNTs have also been fabricated, but they haven't shown desirable mechanical properties due to their random orientation and the poor van der Waals interactions between nanotubes [33]. Nonetheless, their tensile modulus and strength has been improved to 15.4 GPa and 400 MPa respectively when they are formed into layered bucky-paper/epoxy composites [34,35].

In three dimensions, several foam-like structures have been synthesized which take advantage of the remarkable flexibility [36] of individual CNTs to bend without exhibiting structural damage. Super compressible VACNTs have been synthesized and shown to exhibit a foam-like response characterized by three distinct regimes: an initial linear regime, a plateau regime associated with buckling, and finally a densification regime [37]. They possess better compressive strength (~15 MPa) and greater recovery rates (2000 μm s^{-1}) compared to other flexible foams [37]. They have been shown to survive fatigue up to a million compressive cycles at moderate strains of up to 60% [38]. Their mechanical properties, however, are strongly dependent on the synthesis techniques and conditions used, position of the substrate in the furnace, the resultant sample's morphology and density, and any post-treatment applied. For example, fixed- and floating-catalyst CVD synthesis can result in significantly different mechanical properties (a two-orders-of-magnitude difference in effective modulus and yield strength) [39]. The reaction time in the floating catalyst synthesis has been shown to result in different recoveries of the compressed samples (30% recovery for 7 min reaction time vs. 80% recovery for 10 min reaction time) [40]. The position of the substrate along the flow direction has also been shown to play an important role in the bulk density and mechanical properties of the samples synthesized using floating-catalyst synthesis [41]. Similarly, the composition of the gas during synthesis also has been used to tailor the mechanical properties; for example, by changing the concentration of hydrogen in the feedstock for a floating-catalyst system from 0 to 50 percent the compressive strength and hysteretic energy dissipation could be changed by a factor of five [42]. Likewise, post-growth CVD treatment at 750 ^{o}C for varying durations has been shown to result in radial growth of additional walls and, as a result, significantly improved compressive strengths [43].

Very recently, there has been a growing interest in improving the mechanical properties of the VACNT foams by coating them with nanoparticles or thin layer coatings. A post-synthesis coating of MnO_2 nanoparticles has been shown to improve the energy dissipation by over 100% and the loading and unloading moduli by over two times when compared to a control sample [44]. Ceramic coatings (Al_2O_3) between 8.5 and 50 nm thick applied using atomic layer deposition on aligned CNT forests have shown ~1000-fold tunability in Young's modulus, between 14 MPa and 20 GPa [45]. Similarly, amorphous silicon carbide (SiC) coatings of up to 21.4 nm on the CNTs have been shown to improve the compressive strength by three orders of magnitude, from 1 MPa to 1.8 GPa, and can give a modulus of up to 125 GPa [46].

In addition to the continuous foam-like microstructures, several controlled geometries of VACNTs have also been synthesized for different purposes. Diverse 3-D micro-architectures with spatially varying geometries have been fabricated using capillary forming to make master molds for microscale polymer assemblies [47,48] or by controlling growth rates and inducing strain to create curved micro-architectures [49]. These advancements in synthesis have laid further pathways for tuning the stiffness and geometries of VACNT structures and for incorporating biological and chemical functionalities [47]. Similarly, corrugated micro-architectures of VACNTs have been fabricated as out-of-plane micro springs with geometrically tunable compliances [50].

Taking advantage of 1- and 2-D periodicities and geometries, the micro-architectures created using photolithographic techniques and CVD synthesis have shown highly tunable mechanical response and improved properties when compared to continuous VACNT foams, but with densities lower by an order-of-magnitude [51]. Dynamic properties of such micro-architectures of VACNTs are discussed in detail in Chapter 5. These studies suggest that engineering the microstructures by utilizing structural mechanics principles can significantly enhance the already impressive properties of VACNT structures.

Besides the straight CNT structures, helically coiled CNT (HCNT) structures have also been synthesized [52] and shown to exhibit unique mechanical behaviors. For example, the contact interaction of a spherical indenter with HCNT arrays is even more strongly nonlinear than what one would expect from Hertzian-like interactions, and is significantly different from the contact interaction of a spherical indenter with VACNT foams [53]. This highly nonlinear collective response is primarily attributed to the unusual entanglement between neighboring coils and to the collective bending behavior of the coil tips when they are impacted by a spherical indenter [54]. The HCNT foams have been shown to mitigate low velocity (0.2 ms^{-1}) impact forces efficiently and fully recover from deformation of the order ~5 μm (5% strain) [53]. However, the deformation mechanisms and the mechanical response of HCNT foams at high rate large deformation are not yet well understood. A detailed study on the mechanical response of aligned HCNT foams is presented in Chapter 4 of this dissertation.

Apart from aligned CNT structures, sponge-like structures with controlled porosities and low densities have also been fabricated using randomly oriented CNTs. Even though their primary purpose is for environmental applications such as sorption, filtration and separation [55], they also have been shown to present high compressibility of up to 95% of their volume at low stress levels of less than 0.25 MPa, fatigue resistance to repeated compressive cycles (~100 cycles) and high recovery of more than 90% of their deformation upon unloading [55]. Hierarchical agglomerates of CNTs with controlled porosities have also been synthesized for high pressure cushioning [56]. Recently, uniform conformal coatings of amorphous carbon applied on these randomly oriented CNTs with coating thicknesses of between 10 and 30 nm has been shown to improve elasticity by reducing the energy loss during quasistatic cyclic loadings and can sustain ~1000 compression cycles without severe damage [57]. Coating single-walled CNT sponges with graphene has also been shown to improve fatigue resistance, enabling the systems to survive ~2000 cycles at 60% strain and ~1 million cycles at 2% strain without significant permanent damage [58]. The introduction of graphene also improved the Young's modulus and storage modulus of the CNT sponges by a factor of six and the loss modulus by a factor of three [58]. Similarly, CNT aerogels have been synthesized by crosslinking randomly oriented SWCNT bundles using nanoparticles. These have been shown to exhibit high Young's modulus and electrical conductivity compared to other silica and alumina aerogels [59].

1.7 Rate effects on the mechanical response of CNT structures

In this section, a brief summary of rate-effects observed on the CNT structures is presented. The discussion is limited to the CNT structures with foam-like microstructure composed of aligned CNTs or randomly oriented CNTs. So far, studies of rate-effects on the mechanical response of bulk CNT foams have focused on the static (prolonged loadings), quasistatic, or on the linear dynamic regimes.

Long duration (~8 hrs) stress relaxation and creep experiments performed on VACNT arrays have shown nonlinear viscoelasticity [60]. A power law function of time was used to describe the response and it was found that the stress relaxation exponent is nonlinearly dependent on the applied strain level and the creep exponent is nonlinearly dependent on the applied stress level [60]. Creep experiments performed using nano-indentation have also shown viscoelastic response in which the viscoelasticity is dependent on the VACNT density; the strain-rate sensitivity was reduced by a factor of two by doubling the density of the VACNT array [61]. Reduced freedom of movement of the CNTs due to geometry in dense VACNT arrays has been suggested as the cause for the reduced creep deformation [61].

Uniaxial compression cycles performed at up to 80% strain in the quasistatic regime (10^{-4}-10^{-1} s^{-1}) have shown a rate-independent mechanical response [62]. Conversely, a few other studies at faster, but still quasi-static, strain rates (up to 0.04 s^{-1} [63] and up to 1 s^{-1} [64]) have suggested rate-effects on recovery [63] and unloading modulus [63,64]. In both reports the recovery and elastic unloading modulus were shown to increase with increasing deformation rates.

In the linear dynamic regime, uniaxial nano-dynamic mechanical analysis (nano-DMA) at small amplitudes (3-50 nm; 0.7% strain) showed no dependence on the CNT foam's response to the driving frequency [65]. However, they reported the dependence of the storage and loss moduli on the driving amplitude and on the variation of the foam's microstructure. Large amplitude DMA performed in torsion-mode (shear) also exhibited temperature and frequency invariant viscoelasticity between 0.1 to 100 Hz and -196 ^{o}C to 1000 ^{o}C [66]. Coarse-grained molecular dynamics simulations and triboelastic constitutive models have supported these experimental observations [67]. Drop-ball tests performed on VACNT forests demonstrated their ability to mitigate impacts at high-rate deformations [68,69]. However, the deformation behavior and the fundamental dissipative mechanisms at high rates and for finite deformations are not thoroughly understood due to the difficulties in obtaining dynamic displacement measurements with microscale resolution. A comprehensive study of the VACNT foams at high-rate deformations (10^{2}-10^{4} s^{-1}) and the complex rate-effects found in this regime are presented in Chapter 3.

1.8 Carbon nanotube composites

In addition to benefiting from these intriguing mechanical responses and attractive properties of standalone CNT structures, CNTs have also been used as reinforcements in composites to improve the composite properties [70] or combined with other materials to create hybrid structures [71,72]. Since the CNT-based composite literature is as broad as the literature of standalone CNT structures, only a brief introduction is given to show some of the important advancements in CNT-based composites (see the review articles [20,24,70,73–77] and the references therein for further details).

When CNTs are used in a matrix of fiber-reinforced composites to form hierarchical composites, the fiber direction properties haven't shown much improvement, but the matrix dominant properties have improved significantly. For example, the inter-laminar shear strength of woven glass fiber-epoxy composite has been improved by 8-30% by introducing up to 2% (by weight) MWCNTs [78]. Importantly, fracture toughness (mode I & mode II) has been significantly improved by up to 100% by introduction of CNTs in glass fiber-polyester [79] or carbon fiber/epoxy composites [80,81]. As an alternative to modifying the matrix with CNTs, reinforcement fibers grafted with MWCNTs before having been reinforced into the polymer matrix have shown even more improvement in the inter-laminar shear strength (up to 150% in carbon fiber/epoxy [82] or silica fiber/polymethylmethacrylate (PMMA) composites [83]). Likewise, CNTs grown on woven fabric and then used for forming reinforced composites have also shown outstanding enhancement in fracture toughness (348% enhancement), flexural modulus (105%), flexural strength (240%), flexural toughness (524%) and dynamic damping (514%) compared to the control composite samples with no CNTs [84].

The performance of CNT foams has also been improved by introducing polymers into their porous microstructures. Particularly, composites made with aligned CNTs infiltrated with epoxy have been shown to present improved viscoelastic damping properties [85]. The interfacial sliding at polymer-CNT interfaces and the stick-slip sliding at the CNT-CNT interfaces have been suggested as the principle mechanisms for energy dissipation. Similarly, VACNT arrays have been anchored into a thin layer (~50 μm) of polydimethylsiloxane (PDMS) to create single-layer polymer-anchored or multi-layer polymer-anchored assemblies for energy absorbing and impact mitigation purposes [69,72]. These structures have been shown to dissipate energy over 200 times more effectively than commercial polymeric foams of comparable densities [72]. Vertically aligned carbon nanotube (VACNT) reinforced polymer sandwich composites have been shown to display high rigidity and enhanced damping in linear dynamic regimes [86]. Hybrid layered nanocomposites made by intercalating VACNTs into natural inorganic materials and tested in quasistatic compression cycles have shown compressibility of up to 90% of their original heights and ~10 times higher energy absorption than their original components [71].

1.9 Applications of carbon nanotube structures and their composites

Due to the excellent electrical, thermal and mechanical properties [8] of CNTs, macroscale CNT structures and composites have been proposed, or are already in use, for several commercial applications [24,87]. For example, composites made of CNTs find application in load bearing structures, electromagnetic interference shielding packages, wafer carriers for the microelectronics industry, and damping components. As discussed in the section above, the addition of CNT as reinforcement in a matrix improves the fracture toughness, strength, and stiffness of the base material, making composites suitable for load bearing applications. Commercially available premix resins with CNTs (0.1-20% by weight) are used to improve material damping and provide strength at light weights in sporting goods such as tennis racquets, badminton racquets, baseball bats, and bicycle frames; and as structural materials in wind turbine blades, maritime security boat hulls, and aircraft airframes [24]. Similarly CNTs have been used to enhance metals [88]; for example, commercial Al-MWCNT composites are comparable to steel in strength (0.7 – 1 GPa) while having densities (2.6 g cm^{-3}) of one third of that of steel [24]. The energy dissipative characteristics of the CNT sponges and foams can benefit several impact and vibration damping applications [37,53,55].

The multifunctional properties of hierarchical CNT composites are also under investigation for protection against lightning, improving deicing, and allowing structural health monitoring in aircrafts [84,89]. CNTs have also been used in coatings to enhance the coating strength in anti-corrosion coatings and to reduce biofouling of ship hulls, super hydrophobic coatings [90], and thin film heaters for defrosting windows and sidewalks [24]. The porosity of the chemically and mechanically robust networks of CNTs is advantageous for water purification as well, where CNTs are used to electrochemically oxidize organic contaminants, bacteria, and viruses [91,92]. Other proposed applications of CNT structures include thermoacoustic projectors for underwater sound generation [93], optoacoustic lenses for focused ultrasound generation and high-precision targeted therapy [94], highly elastomeric electrodes [32], bulletproof tough textiles, and conductive electronic fabrics [95,96].