

Chapter 2

Carbon Nanofibers: Structure and Fabrication

Abstract In this chapter, vapor-grown and electrospun carbon nanofibers (CNFs) are emphasized. Fabrication processes and surface modification methods for CNFs are presented. Microstructure of CNFs is discussed based on the reported observations in various studies. CNFs have a complex structure compared to the structure of carbon nanotubes. The orientation of carbon layers in CNFs affects their mechanical properties. Experimental analyses and resulting trends are discussed from various published works, such as studies that investigate the tensile and flexural properties of individual CNFs. The range of measured properties is rather wide, which is likely due to the difference in the structure of the fibers that were tested and the presence of defects. Molecular dynamic simulation results on single nanofibers are also presented to understand their potential of reinforcing composites.

Keywords Carbon • Nanofibers • Nanotube • Vapor-grown • Electrospinning • Polyacrylonitrile • Molecular dynamics

The potential of using carbon-based nanofibers as reinforcement has been recognized since the 1980s for both vapor-grown [1] and polyacrylonitrile (PAN)-based [2] carbon fibers, among other fiber types. Obtaining control over the fiber properties through manipulation of process parameters was of great interest during earlier studies. A similar trend was observed with the development of CNFs. The research continued with measuring the properties of single CNFs and then with synthesis and characterization of CNF reinforced composites. Modeling and simulation studies were useful in understanding the nature of CNFs and in understanding the potential benefits of using such nanofibers in composites. Comprehensive literature reviews highlighting the mechanical properties of CNF-reinforced polymer composites have been previously published [3–6]. These reviews can be of great help in developing the background of CNF reinforced composites.

2.1 Structure and Fabrication

CNFs have been classified as linear, sp^2 -based (one double bond, with two single bond) discontinuous filaments, where the aspect ratio is greater than 100 [7]. Transmission electron microscopy (TEM) revealed that the layers of graphitic planes of most CNFs are generally not aligned along the axis of the fiber. Nanoscale filaments such as CNFs have even been classified in previous works as follows, depending on the angle of the graphene layers that compose the filament [8]:

- Stacked (graphene layers stacked perpendicular to the fiber axis)
- Herringbone/Cup-stacked (graphene layers stacked at an angle between parallel and perpendicular to the fiber axis).

These layering arrangements are possible, due to the growth mechanism of the CNF that depends on the geometric facets of a metallic catalyst particle and the gaseous carbon feedstock (hydrocarbon or CO gas) that is introduced during CNF processing. Such general classifications leave further room for additional categories of carbon-based nanoscale fibers; however, the discussion will be limited to the more common types known henceforth as vapor-grown CNFs (VGCNFs) and electrospun CNFs (ECNFs). The inherent structure of CNFs is usually dependent on the production processes employed, as described in the following sections for both VGCNFs and ECNFs.

2.1.1 Vapor Grown CNFs

The structure of VGCNFs resembles graphene layers helically folded along the axis of the fiber, providing a hollow core. The graphitic layers are folded at an angle to the fiber axis, giving the appearance of cups that are layered, or “stacked” one on top of the other along an axis, as shown in the simplified diagrams of Fig. 2.1 [6, 9]. Such a “cup-stacked” structure distinguishes them from CNTs, which have the appearance of a single cylinder or multiple concentric cylinders made of graphene layers oriented parallel to the CNT axis. An available TEM image demonstrates unfurling of a graphene layer in a CNF, as shown in Fig. 2.2 [10], thereby providing direct visual evidence and confirming the continuity of the stacked layers in the form of helical folding. The hollow core graphitic inner layer and a turbostratic carbon outer layer structure are further shown in high resolution TEM images in Fig. 2.3. The current literature has attempted to develop a practical definition of CNFs by stating that carbon-based nanofibrous structures with nonzero angles with respect to the fiber axis are to be deemed as CNFs [8, 11, 12].

The structure and properties of VGCNFs are influenced by their fabrication process. The processes that are used for CNF production have been around since the 1970s for producing other materials and have been adapted for CNF

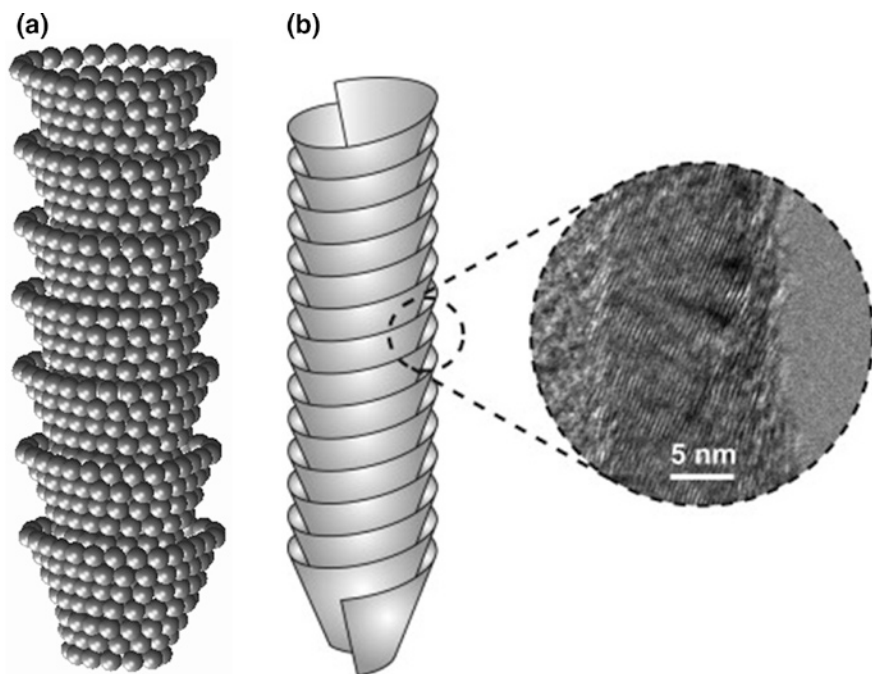


Fig. 2.1 **a** 3D CAD rendering of cup-stacked graphene layers in a single CNF, and **b** Simplified schematic of stacked-cup carbon nanofiber helical structure with *inset* in **(b)** showing TEM image of inclined orientation of grapheme planes along the side of structure with respect to nanofiber axis. Image taken with permission from [9]

production in the recent years [1, 6, 8]. Chemical vapor deposition (CVD) is among the most common processes used for producing VGCNFs. Transition metal catalytic particles such as iron, nickel, cobalt, and copper are utilized in conjunction with a carbon supply, such as carbon monoxide or a hydrocarbon gas, at temperatures ranging from 500 to 1200 °C in the CVD process [13]. The size of the catalyst particle determines the size of the graphitic structure of CNFs [14]. Several models have been proposed to explain the growth of the graphitic structure through the use of metal catalysts [15, 16]. The size of the catalyst particles is usually in the range 10–100 nm, which determines the outer diameter of the CNFs produced [8, 16]. The angle at which the “cups” are oriented strongly affects the properties of CNFs [8, 17, 18]. A faceted catalyst particle may allow for the formation of angled layers where graphitic platelets are deposited at an angle leading to growth of CNFs. A simple schematic illustration of this process is shown in Fig. 2.4a. In contrast, a spherical catalyst particle results in graphitic layers which are parallel to the growth axis, allowing for the formation of single-walled or multi-walled CNTs [7, 8]. Experimental analyses on CNFs denoting the effect of varying cone angles are not yet available. However, atomistic simulations have revealed that the fiber stiffness and failure mode are a function of cone angle,

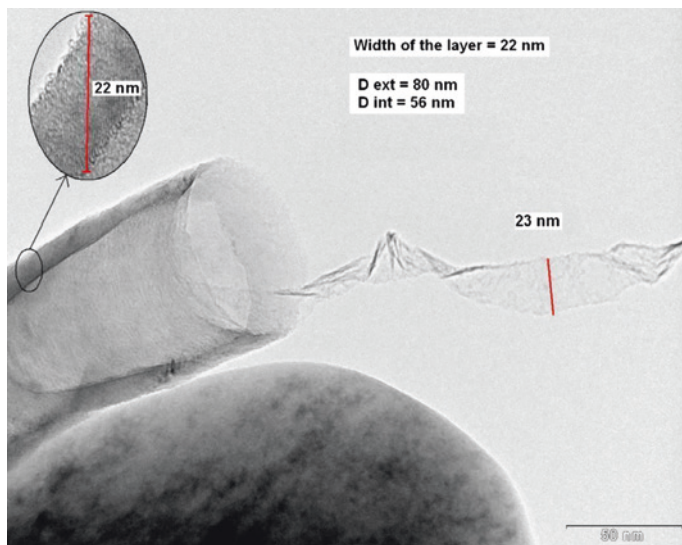


Fig. 2.2 TEM image of the unfurling of one end of a VGCNF. The continuity of the fiber explained the electrical conductivity of the nanofibers in previous studies. Image taken with permission from [10]

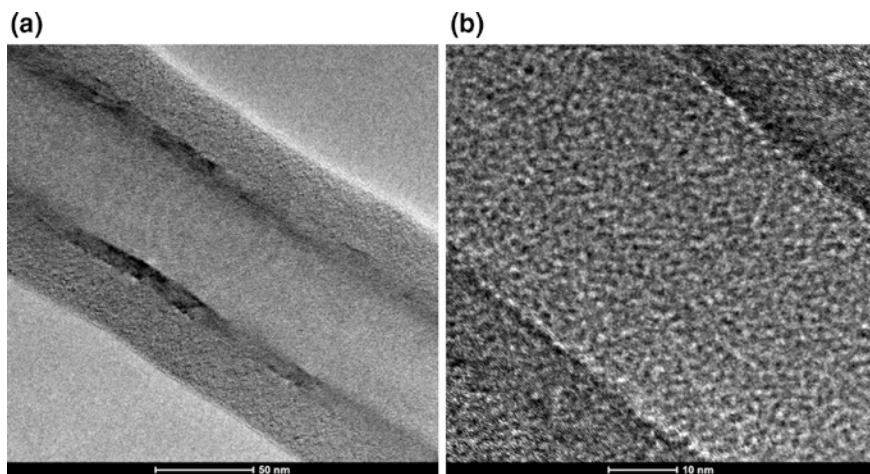


Fig. 2.3 **a** TEM images of a single VGCNF with a hollow core, inner graphitic layers, and outer turbostratic carbon layers. **b** Higher magnification TEM micrograph of hollow core structure surrounded by carbon layers

which can vary within a rather large range (38.9° – 112.9°) [18]. Advances in CVD-based methods, such as plasma-enhanced CVD, allow for use of glow discharge plasma for production of carbon nanostructures at considerably lower temperatures ($T \geq 650^{\circ}\text{C}$) than traditional CVD methods [12].

2.1.2 Electrospun CNFs (ECNFs)

An alternate route to the production of CNFs is through electrospinning [19]. The electrospinning process is schematically illustrated in Fig. 2.4b. A fine tip needle syringe is used in this sol–gel process. High voltage is applied to the droplet at the tip of the needle, which causes the solution to spurt out from the needle to a target. When the surface tension is high enough for the solution to prevent breaking into a fine droplet, a fibrous structure is developed and collected at the target. Polymeric precursors used in this process have included PAN, cellulose, and pitch, where PAN is the most desirable and most often used due to its higher carbon yield and strength [7, 20], as well as its ease of fabrication and mass-production [19, 21].

A heterogeneous “skin-core” structure is observed in ECNF in Fig. 2.5, where the carbon layers are oriented radially along the fiber skin, but a randomized granular structure is observed along the axis of the fiber core [22]. It is proposed that the skin–core structure is formed because of shear forces exerted on the fiber due to the variation in inner and outer fiber temperatures encountered during the electrospinning process [23].

2.1.3 Comparison of VGCNFs and ECNFs

The CVD process generally tends to yield ultra-high modulus CNFs [7, 24]. However, a significant amount of catalyst residue, relatively lower product yield, and use of expensive equipment are the limitations of the CVD process [19]. Compared to the “bottom-up” method of production employed by CVD, electrospinning takes advantage of its “top-down” manufacturing process, which facilitates production, assemblage, and alignment [21]. The CVD process produces fibers that are difficult to align without the use of magnetophoretic or

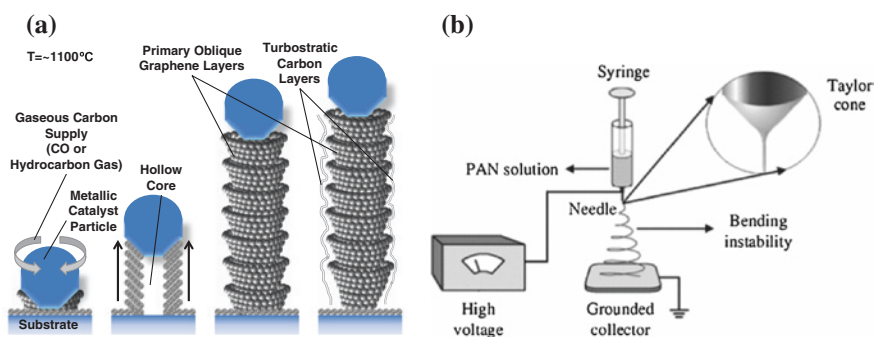


Fig. 2.4 **a** Schematic of chemical vapor deposition (CVD) process with illustration of CNF layering, and **b** Schematic of electrospinning of PAN fibers, which is typically followed by stabilization and carbonization to create CNFs. Image taken with permission from [19]

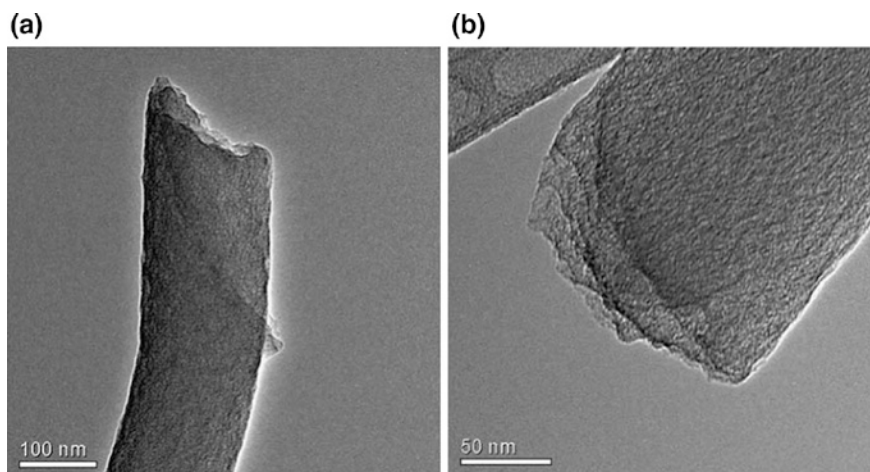


Fig. 2.5 TEM micrographs of broken *edges* of carbonized ECNFs with **a** loosened outermost layer, and **b** several sheath layers can be observed at the edge. Images taken with permission from [22]

electrophoretic methods, as well as mechanical methods such as screw extrusion [25–27]. Both methods of CNF production are continuously refined to efficiently produce higher CNF yields for mass production.

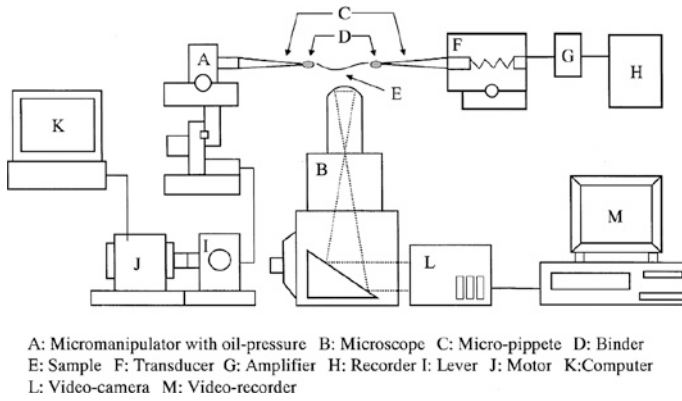
Due to the heterogeneity of the skin–core structure of ECNFs, the cup-stacked structure of VGCNFs offers distinct advantages with respect to mechanical properties. However, the crystallinity of the ECNF structure can be manipulated through further high-temperature carbonization, thus prompting enhancements in mechanical strength. The strength and modulus values of both types of CNFs are discussed in detail in the following section.

2.2 Measured Mechanical Properties of CNFs

Direct measurements of mechanical properties were conducted on individual CNFs [4, 22, 24, 28–31]. Analytical predictions and finite element simulations require such values for validation and to analyze associated data trends and mechanisms of composite reinforcement using CNFs [6, 17, 18, 32–35]. Table 2.1 lists experimental measurements of strength and modulus of CNFs. The mechanical properties of both VGCNF and ECNF are found to be functions of processing methods, fiber diameter, and type of loading used for mechanical analysis. The tensile strength of VGCNFs was measured through the use of a micromanipulator that is viewed under a high-speed camera and a scanning electron microscope, shown in Fig. 2.6 [24]. Later studies involving graphitized ECNF bundles derived from PAN tested tensile strength using computer controlled mechanical testers,

Table 2.1 Experimentally measured strength and modulus values of CNFs

Author	Process ^a	Diameter (nm)	Loading type	Strength (GPa)	Modulus (GPa)
Endo et al. [24]	VG	300–1000	Tensile	1.25–3	100–300
Ozkan et al. [28]	VG ^b	150	Tensile	2.35–2.9	180–245
Lawrence et al. [36]	VG	115–470	Bending	n/a	6–207
Zhou et al. [21]	E ^b	300	Tensile	0.597–0.969	n/a
Arshad et al. [20]	E	150–500	Tensile	1.86–3.52	80–191
Zussman et al. [22]	E	50–250	Bending	0.55–0.71	53.5–75.3

^aVG: vapor grown, E: electrospun^bIncludes functionalized/graphitized CNF**Fig. 2.6** Schematic of micromanipulator setup utilized for tensile tests on VGCNFs. Image taken with permission from [24]

where it was found that the use of phosphoric acid enhanced the strength of graphitized ECNF by 62.3 % [21]. Ordered, graphitic, ribbon-like structures were also induced in the ECNF through sufficient graphitization at 2200 °C in vacuum in addition to phosphoric acid content to manipulate the tensile strength [21].

Bending experiments provided consistent results through the use of the mechanical resonance method, which entailed clamping a PAN-based nanofiber to the cantilever tip of an AFM and driving it to its fundamental resonance by a piezoelectric actuator [22], as shown in Fig. 2.7a. Using a modulus-frequency relationship from classical linear elasticity, the modulus can be obtained by [22]

$$f_n = \frac{\beta_n^2 d}{2\pi L^2} \sqrt{\frac{E}{16\rho}} \quad (2.1)$$

where E is the Young's modulus, which in this case is termed as the effective bending modulus, due to the fiber measurement method utilized. β_n is the eigenvalue obtained from the characteristic equation $\cosh(\beta_n) \cos(\beta_n) = -1$, and d , L ,

and ρ represent diameter, length, and density of the fiber, respectively. Three-point bend tests on VGCNFs have also been implemented using AFM probes, with platinum pads used as additional constraints, thus yielding CNF modulus values as high as 207 GPa [36]. In such studies, it was observed that the midspan deflection δ of the individual CNF varied linearly with the applied force F , which is consistent with classical beam theory. Therefore, the elastic modulus can be obtained from the AFM cantilever setup through [36]

$$F = \frac{192EI}{L^3}\delta \quad (2.2)$$

where E , I , and L are the elastic modulus, second moment of the cross-sectional area, and the span of the beam, respectively. The range of bending modulus values for ECNFs is observed to be generally smaller than the range of values obtained from testing vapor-grown fibers, where the bending modulus of VGCNF can vary by one to two orders of magnitude [36].

Platinum constraints were later utilized in a microelectromechanical system-based (MEMS) experimental setup to observe the strength, modulus, and fracture characteristics of individual VGCNFs [28]. An example of a MEMS-based tensile test setup can be observed in Fig. 2.7b. Experimental studies on PAN-based CNFs observed tensile strength of CNFs as a function of carbonization temperature using MEMS-based loading setups [20]. The results derived from such MEMS-based experimental setups showed some of the highest measured tensile strength values for either VGCNFs or ECNFs listed in Table 2.1. However, the disparity of values in Table 2.1 remains highly dependent on the process method, fiber diameter, loading type, and possibly the structure of CNF. For example, it is shown in Table 2.1 that typical PAN-derived ECNFs attain mechanical properties lower than that of VGCNF, which is likely due to the differences between the VGCNF and the ECNF structure. It is observed in earlier studies that the discontinuous granular core morphology observed for the skin-core structure of ECNF offers a limited

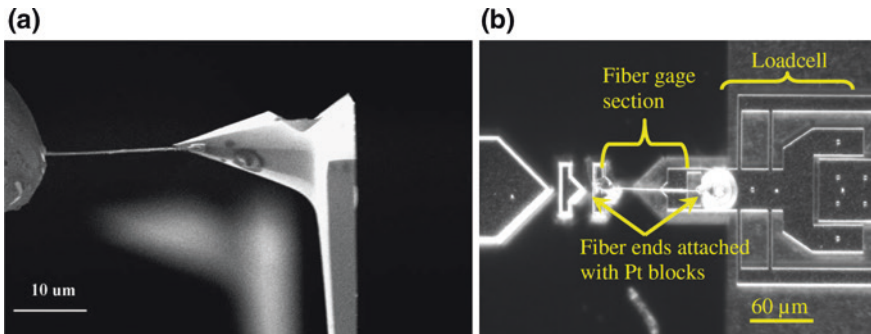


Fig. 2.7 **a** A single ECNF constrained between a tungsten wire (*left*) and an AFM tip (*right*) [22]. **b** A MEMS-based tensile measurement platform utilizing platinum blocks to constrain a single VGCNF. Images taken with permission from [28]

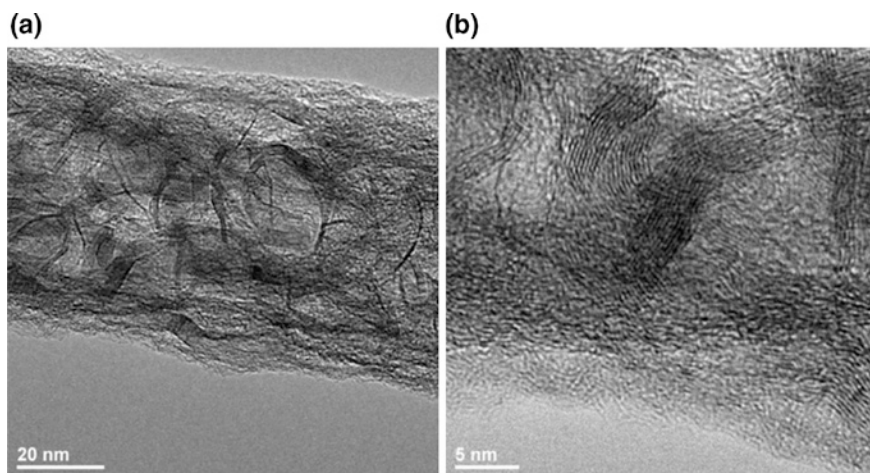


Fig. 2.8 **a** TEM image of ECNF carbonized at 1400 °C and **b** close-up TEM image of carbon crystallites abundant in the ECNF structure. Images taken with permission from [20]

range of mechanical strength at processing temperatures of up to 1100 °C [21]. However, further research on carbonization effects due to higher temperature processing has allowed for increased strength in ECNF, where non-carbon elements are removed from the ECNF structure, and the appearance of carbon crystallites allowed for increased densification and strengthening of individual fibers as shown in Fig. 2.8. With such processing capabilities, the mechanical properties of ECNF can be made comparable to VGCNF. The tensile strength and modulus values are compared with respect to treated temperatures in Fig. 2.9. It can be observed that the tensile strength of ECNFs at 1400 °C is 21.3 % higher than the maximum value of average tensile strength of VGCNFs obtained in [28]. However, large portions of the standard deviations recorded from the studies coincide with each other, resulting in mechanical property data that is comparable to both types of CNFs.

An inverse relationship is noted between the fiber diameter and the modulus in Table 2.1, which may be due to the significance of shear deformation as the aspect ratio changes [37]. Other size effects are also likely, given that CNFs with larger dimensions have a higher chance of containing flaws and defects adversely affecting their strength [12]. Such size effects are found to be prevalent for studies analyzing both ECNFs [23] and VGCNFs [28], as evidenced by the range of values in Table 2.1. Additionally, the aforementioned studies that obtained strength and modulus measurements using MEMS-based devices are comparable in terms of tensile strength ranges. However, the modulus was measured to be as low as 180 GPa for VGCNFs [28], whereas modulus values obtained from testing PAN-derived CNFs were as low as 80 GPa [20]. Additionally, within the set of modulus values of ECNFs shown in Table 2.1, the bending modulus is up to one order of magnitude lower than the values obtained from tensile testing of PAN-based CNF.

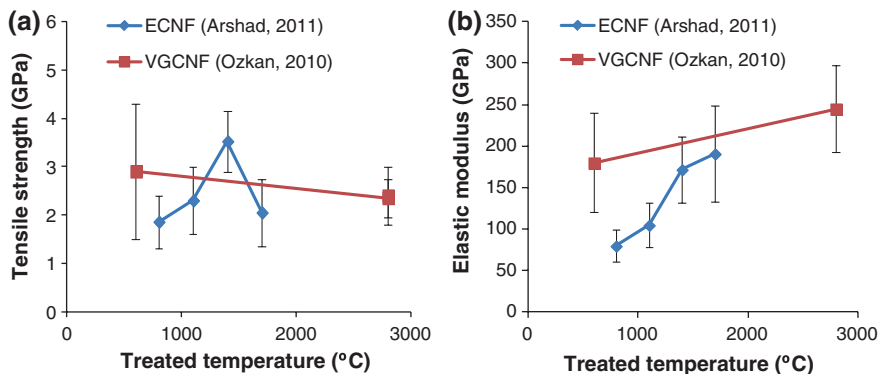


Fig. 2.9 Comparison graphs of **a** tensile strength and **b** elastic modulus with respect to treatment temperature of ECNF and VGCNF (data derived from [20, 28])

2.3 CNF Surface Enhancement

Efficient utilization of CNFs within composites is required for realizing their potential as reinforcement. Considerations of the CNF aspect ratio [38, 39], proper CNF dispersion within various matrices [40, 41], and rate of mechanical loading of composites containing CNFs [35, 42] have been explored extensively in an effort to identify factors for variation in composite mechanical performance. However, enhancement of CNF itself can also play an important role in the improvement of mechanical properties of the composite. Enhancements through fiber functionalization and graphitization have allowed for improvements in mechanical properties of VGCNF [28] and ECNF [21], respectively, as denoted in Table 2.1. Additives incorporated in the precursor during fabrication, such as phosphoric acid, have proven to be useful in enhancing the strength of PAN-based CNFs by facilitating the formation of graphitic structures within the CNFs [21], where such ordered graphitic structures have allowed for crystallinity and mechanical property improvements.

Functionalized CNFs can allow for the formation of chemical bonds and improve compatibility with polymer matrices [43–47]. For experimental inclusion in composites, CNFs have been treated with acid-based chemical reagents [47]. Functionalization is more common for VGCNFs compared to ECNFs, although acid-based chemicals such as heteropolyacids have been incorporated into PAN matrices during ECNF production to enhance fiber morphology and physicochemical properties [48]. Molecular dynamics simulations have captured the effect of pristine [47] and functionalized [50] CNFs on the crosslink density around the nanofiber within a vinyl ester polymeric resin. It was shown that an interphase region with a lower crosslink density forms around a pristine CNF, where different chemical concentrations near the surface of functionalized CNF form a stiffer interphase region with a higher crosslink density [49, 50]. Such results can be useful to further modify the properties of multiscale composites through improved fiber–matrix interactions [50].

Adhesion between the functionalized VGCNF surface and a polymer matrix has been improved through the chemical grafting of a polymer on the fiber surface [43, 51]. In situ intercalated polymerization is the primary mechanism through which a polymer layer can be introduced on a functionalized CNF surface, where polymerization occurs inside of a composite on a functionalized surface in the presence of filler. Therefore, such materials have been dubbed in situ polymer nanocomposites, a topic which has been discussed in the published literature [52]. However, the quantity of the chemical that is grafted onto CNF and ultimately introduced into the solid multiscale composite is often difficult to parameterize in terms of composite constituent percentage through direct measurement and pre-determination of composite material design. Such assessments become crucial in determining the effect of variation of weight or volume percentage of chemical additive on the mechanical properties of the individual CNF and the composite. Thus, for the purposes of this review, in situ composites developed through functionalization of CNF will only be given general mention. Such studies on CNF enhancement can lead to mechanical property and dispersion improvements while reducing the amount of CNF reinforcement necessary, thus facilitating composite fabrication, CNF dispersion, and ultimately reducing cost.

2.4 Modeling of Mechanical Properties of CNF

Before direct experimental measurements were conducted, iterative back-calculation and semi-empirical estimations, as well as analytical predictions and finite element simulations, were employed to obtain predictions for values of modulus of CNFs [6, 17, 18, 33, 34]. Such methods allowed using predicted properties of CNFs in estimating the properties of CNF reinforced nanocomposites before the actual experimental measurements on single CNFs were possible [32, 35]. For the majority of simulation studies performed on individual CNFs, the cup-stacked structure of VGCNFs is most commonly utilized, as opposed to the more heterogeneous and randomized structure found in ECNFs.

It has been previously proposed that the graphitic cone angle and layer alignment directly influence the mechanical properties of individual CNFs [6]. Initial attempts at developing analytical solutions have demonstrated that variation in the CNF length and cup tilting angles with respect to the fiber axis can affect the Young's modulus [17]. This was determined through the derivation of an analytical relationship between the Young's modulus of a single-shell nanocone (Y_{CONE}) within a VGCNF and a single-walled CNT (Y_{SWCNT}), as follows:

$$Y_{\text{CONE}} = Y_{\text{SWCNT}} \cos^4 \theta \left(1 - \gamma_{\parallel} \sin^2 \theta\right)^2 \quad (2.3)$$

where $\gamma_{\parallel}$ is the Poisson's ratio along the graphene plane and θ is the tilting angle of the graphene plane with respect to the cone axis. Since a single CNF can be comprised of N shells of nanocones, the total strain energy E of a single CNF is defined as [17]:

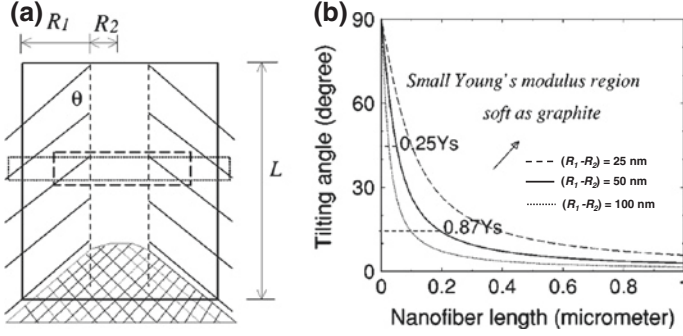


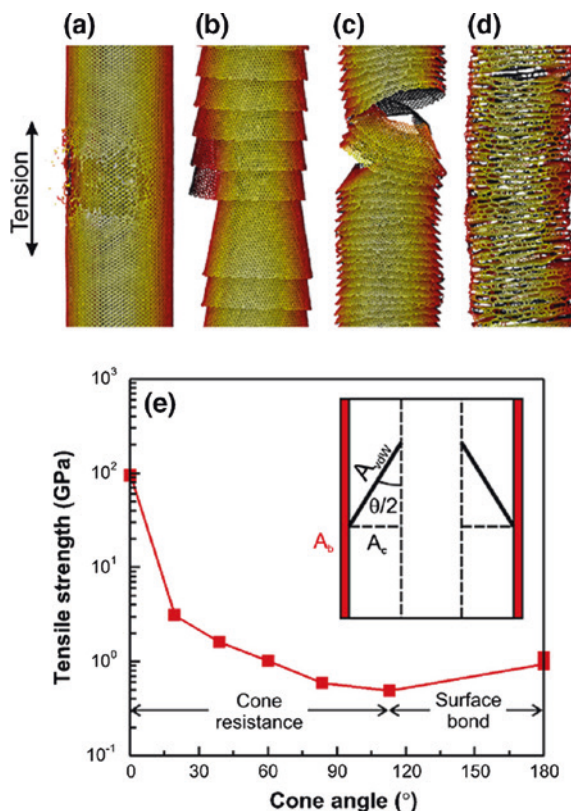
Fig. 2.10 **a** Schematic denoting CNF geometric parameters. **b** Plot demonstrating relationship between the geometric parameters and Young's modulus of single CNFs, where θ is the tilting angle, L is the nanofiber length, and R_1 and R_2 are the outer and inner radii of the CNF, respectively. Images taken with permission from [17]

$$E = AL \frac{1}{2} Y \varepsilon^2 = \sum_{i=1}^N E_{\text{shell}}^i + \sum_{i=1}^{N-1} E_{\text{VDW}}^{i,i+1} \quad (2.4)$$

where Y , A , L , and ε are the Young's modulus, cross-sectional area, fiber length, and fiber strain, respectively. The first summation term takes into account the strain energy of all shells, where the strain energy of the i^{th} shell is denoted as E_{shell}^i . The second summation term takes into account the total strain energy contribution of the van der Waals (VDW) forces acting between each shell, where the VDW strain energy acting between shells i and $i + 1$ is denoted as $E_{\text{VDW}}^{i,i+1}$. Using Eq. 2.4, the Young's modulus of a CNF composed of N shells can be derived so that the relationship between the Young's modulus and parameters, such as the cone tilting angle and nanofiber length, can be assessed as shown in Fig. 2.10a. Asymptotic trends are observed in Fig. 2.10b for the modulus with respect to these two parameters. Low tilting angles, low nanofiber lengths, and larger differences between the inner and outer radii of CNF allow for higher modulus. Such expressions and trends derived in [17] were validated with molecular dynamic (MD) simulations utilizing single-shell, four-shell, and seven-shell CNF nanocones.

Computer models have expanded on the structure of helical nanostructures such as CNF [53], where consideration of carbon atomic bonds mapped as a hexagonal structure can potentially show accurate visual demonstrations of CNF growth and facilitate calculation of physical properties. Recent MD simulations on cup-stacked CNFs have further explored the role of the cone angle [18]. Figure 2.11 shows that maximum strength is achieved when the cone angles in a CNF are close to being parallel to the fiber axis, such as in a CNT, where failure modes are shown to vary with cone angle in Fig. 2.11a–d. A tensile strength minimum is also observed at a critical cone angle in Fig. 2.11e, thereby demonstrating competition between van der Waals forces and strengthening mechanisms from

Fig. 2.11 MD simulations of **a** SWCNT, and CNF models with *cones* at **b** 19.2° , **c** 83.6° , and **d** 180° . **e** Log-scale relationship between tensile strength and cone angle. Images taken with permission from [18]



thermal-induced surface bonds [18, 34]. However, it must be noted that direct experimental studies on the effect of the cone angle on the mechanical properties of single CNFs are scarce at present.

2.5 Summary

Vapor-grown and electrospun CNFs are discussed in this chapter. The manufacturing processes for both types of CNFs are discussed. VGCNFs usually have a helically folded or stacked-cup geometry, whereas ECNFs have a core-shell structure. The difference in their structure reflects in the difference in their properties. Studies are now available that have tested single CNFs for mechanical properties, usually under tensile and bending loading. The experimentally measured strength is found to be in the range 550 MPa–3.5 GPa. A similarly large scatter is observed in the modulus values, which vary from 53 to 300 GPa under tensile loading. Surface modification can help in making CNFs compatible with the matrix polymer. MD simulations have been used extensively to estimate the

properties of CNFs and also to understand the deformation mechanisms and trends in mechanical properties with respect to parameters such as cone angle and fiber diameter. Such studies have been very useful in providing insight into CNFs because of a lack of direct observations at that scale.

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