Chapter

Multifunctional Carbon Nanotube Reinforced Polymer/Fiber Composites: Fiber-Based Integration and Properties

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Abstract

Carbon nanotubes are one of the most versatile nanomaterials currently used to modify the properties of both thermoplastic and thermoset-based composites, both with and without the use of a fibrous reinforcement phase. Electrically and thermally conductive by nature, their addition to traditional fiber-reinforced polymer composites has not only heralded increased mechanical properties in terms of flexural, tensile, impact, and interlaminar properties, but also allowed imparting inherent conductivity to the final composites, allowing the creation of specialized, isotropic, anisotropic, and hierarchically graded composites with applications ranging from self-diagnostic damage detection, de-icing to energy storage and conversion. The purpose of this book chapter is to focus on the methods used to integrate carbon nanotubes, both anistropically and anisotropically via techniques that focus solely on the fibrous reinforcement phase and not the matrix, into fiber-reinforced polymer composite materials. The chapter aims to review the properties that may result from such integration of the various techniques, provide a current state of the art of the multifunctional properties, which have been achieved thus far, and outline possible future dimensions of investigation and application.

Keywords: carbon nanotube, nanocomposite, fiber reinforcement, fiber-reinforced polymer, glass fiber, carbon fiber, functional composite

1. Introduction

Carbon nanotubes (CNTs) are one of the few materials that have found a plethora of applications in almost all fields, stemming from their exceptional inherent properties. Being inherently electrically and thermally conductive [1–3], showing relatively high stability in elevated temperatures [3, 4], and having the ability to be integrated with a wide variety of materials [5] while showing a level of chemical inertness [6], CNTs are probably one of the most widely investigated nanomaterials for applications in their pure form, in macrostructures, or when combined to form nanocomposites.

The term CNT is a generalization, which encompasses the three most widespread forms of this material, categorized by the number of walls shown by the tubes, as shown in **Figure 1**. CNTs may display single (SWCNT), double (DWCNT), or multiple walls (MWCNT, more than 2), which in effect causes changes to their properties, hence the further categorization [7]. CNTs may also be classified according their ends being opened or closed [8], by their electronic structure and properties [9], or by additional features added to their structure during synthesis [10]. However, one trend remains: reducing the number of walls displayed by the CNTs with the length remaining constant, or by keeping the diameter constant and increasing the length, increases the aspect ratio of the CNTs [11]. This is inherently important for CNT/polymer nanocomposites since percolation theory and percolative behavior are entirely dependent on this ratio [12]. Almost all bulk functional properties are dependent upon dispersion, the percolation network, and its formation and manipulation [12–14].

All polymer composite materials consist of two distinct phases: the matrix material, generally comprising the polymer itself, and the reinforcement material, which may be particulate or fibrous in nature. Since this book chapter deals with fiber-reinforced polymer composites (FRPCs), this chapter shall focus on elaborating on the fibrous reinforcement phase. As stated, FRPCs are made up of two distinct phases, and, thus, two distinct approaches to including CNTs into FRPCs exist: the first being through modifying the matrix material and the second integrating CNTs on the fibrous reinforcement phase. Although this chapter is dedicated to the latter approach, it is necessary to lightly touch upon the former to draw comparisons and be able to compare the advantages and disadvantages of the two.

Integrating CNTs into matrix materials is the more popular approach when literature for the topic is reviewed, both for thermoset [15–18] and thermoplastic polymer nanocomposites [19–23]. In this method, CNTs are dispersed within the polymer matrix to obtain either homogeneous or heterogeneous dispersion of structures [24]. Following this modification of the polymer phase of the composite, this dispersion is then used and transferred to the fibrous reinforcement phase, by method such as vacuum infusion [25], resin transfer molding [26], injection molding [27], compression molding [19], extrusion [28], and pultrusion [29], depending upon the type of polymer and fibers used. Integrating CNTs through the matrix is extremely popular since it relies on cheaper processing equipment, is facile and robust, can be combined with other nanomaterials to form complex composites without major changes to processing regimes; moreover, it can be used with predispersed masterbatches, and the quality of the percolation network is dependent

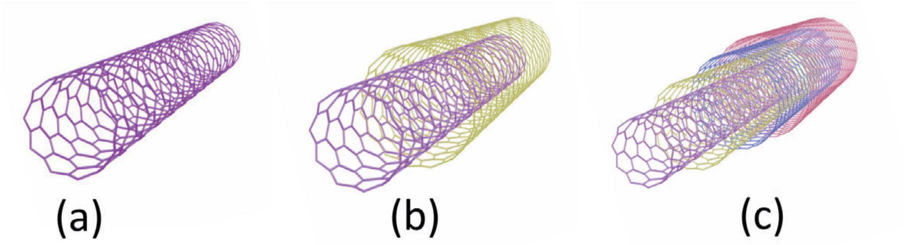

Figure 1.
The structures of CNTs, most commonly used for classification; (a) SWCNT, (b) DWCNT, and (c) MWCNT.

upon processing parameters, which can easily be optimized. This method has been shown to successfully be used for improving mechanical properties [30, 31], while promoting multifunctionality such as flame retardancy [32], electrical conductivity [15, 19], thermal conductivity [16, 33], piezoresistive response [15, 34], self-detection of damage [35], increased wear resistance [36], and improved fracture and failure resistance [37, 38].

However, the technique has some drawbacks. Due to the fact that high-performance composites usually use continuous fibers as the reinforcement material, it is common for nanoparticles such as CNTs to be "filtered" by the fibers, causing uneven distribution of the nano-reinforcements, in turn causing regions of inhomogeneity [39, 40]. Also, since matrix integration usually employs ultrasonication in one form or another, the CNTs become susceptible to damage and loss in properties [41], and the same is seen for some forms of mechanical dispersion [42, 43]. The addition of CNTs to polymer matrices greatly increases the viscosity of the matrix while processing [44], leading to the need for more expensive and high-tech machinery to obtain optimum dispersion and higher weight percentages [45, 46], not to mention a decreased amount of fiber wetting. The addition of CNTs to the polymer matrix may also negatively influence the polymerization degree, causing a loss in mechanical properties [47, 48].

Considering these drawbacks, fiber-based techniques, although more intensive than matrix-based in terms of capital and technological investment, may have certain advantages for large-scale production. The following sections elaborate on the techniques included in fiber-based integration, their advantages and drawbacks, current status of selected results, and possible future implications and directions.

2. Fiber-based CNT integration

2.1 Integration techniques

As stated in the introduction, the integration of CNTs into composites to form nanocomposites by deposition on fibers holds several advantages over the alternative technique. Through this approach, CNTs are not subjected to the filtration effect associated with matrix-based composite manufacturing techniques. Secondly, the CNTs, which are already deposited onto the fibers, allow for a strong interfacial connection between the matrix and the fibers [49]. In addition, although the curing of the matrix may be affected by the CNTs themselves in the local vicinity, this effect is theoretically lower than for homogeneously dispersed CNT/polymer nanocomposites, where the entire volume of the polymer may be affected. By using the fibers as the integrating material, specialized hierarchical composites where directional alignment of CNTs is maintained allow for anisotropic properties to be obtained [50]. Fiber-based integration techniques may roughly be broken down into the following categories: (1) direct deposition of CNTs on the fibers from the CNT source or by direct growth on the fibers, (2) deposition of CNTs via the spray technique, (3) dip coating, and (4) dry transfer of CNTs to the fibers. Additional techniques, which have been shown to be successful in transferring CNTs on the other types of materials, include using a doctor blade for direction alignment and thin film creation [51], the Meyer rod technique for creating thin films [52], slot casting for creating continuous layers with a matrix [53], and inkjet printing [54]. Since these latter mentioned techniques either have not found widespread usage in large-scale fiber-reinforced composite manufacturing or application, or rely on a matrix to be present and retained, they have not been discussed in great detail in the further sections.

2.2 Direct deposition and growth

In this method of CNT deposition, CNTs are deposited directly on the fibers of FRCPs from the CNT reactor, as shown in **Figure 2**. In essence, instead of CNTs being collected on a filter substrate as is normally done, the fibers act as the substrate and collect the CNTs directly onto their surface [55]. This technique is, however, the most complicated and least scalable of the techniques associated with fiber-based CNT integration. Among a few of the problems associated with this technique are enlarging the collection area in the reactor to be able to place the fibers, the fact that control of the flow rate for CNT production to the reactor needs understanding and mastering of the complex ensemble flow of the precursors, catalyst and reactor design, as well as flow tuning for CNT production to the reactor (without additional reactor modifications) [56–60]. This makes controlling the area of deposition troublesome and requiring detailed knowledge of CNT synthesis parameters.

A more intriguing method, whereby a catalyst is deposited on fibers, which are then subjected to reactor conditions to grow CNTs directly on the fibers, was deemed to be more suitable as it allowed passing the fibers through a portion of the reactor, allowing increased controllability of deposition without the need for upscaling the reactor itself [61]. The technique has been investigated by a number of authors all showing the feasibility of growing CNTs directly on the fibers through catalyst deposition, CVD variable adjustment, or a combination of both [62, 63].

Studies utilizing this technique have shown that growth on fibrous substrates can successfully be performed while providing a number of multifunctional properties [64, 65]. He *et al.* showed that the technique, when applied in various configurations, could lead to directionally anisotropic conductivity, with up to eight times in difference according to directions [55]. Rahmanian *et al.* successfully grew vertically aligned CNTs [62], which have been shown to provide increased interlaminar adhesion and strengthening in other publications [66, 67], as well as the ability to detect

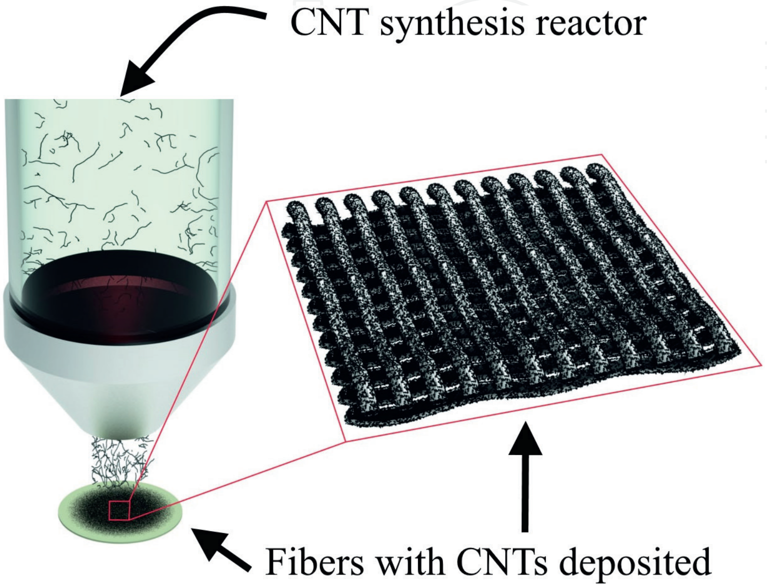

Figure 2.
Direct deposition of CNTs onto fibers with a CNT reactor.

polymerization degree based on piezoresistive response [68]. Zhao *et al.* used a novel flame synthesis technique to grow CNTs directly on glass fibers, resulting in an electrical conductivity increase of more than 10 magnitudes with a simultaneous reported maximum thermal conductivity of ~0.5 W/mK [69]. Pozegic *et al.* showed that by growing CNTs directly on fibers, they were able to enhance the electrical conductivity of the final composite made via vacuum infusion, leading to electrical conductivity enhancement of up to 450%, with potential applications in lightning strike damage mitigation and de-icing in the aerospace industry [70]. The same authors showed that the technique results in no major loss in infusion ability, ~140% increase in Young's modulus, 20% increase in ultimate shear stress, and 83% increase in the initial fracture toughness of the final composites [71]. Veedu *et al.* reported that this method of CNT introduction into FRCPs resulted in lower flexural deflection, higher flexural modulus, strength and toughness (105, 240, and 524% increase), higher interlaminar fracture toughness (~350% improvement), a shear sliding fracture toughness of 54%, all the while showing a thermal and electrical conductivity increase of 151% and roughly 5 magnitudes, respectively [72]. Further studies in the field have shown that the growth on fibers allows not only mechanical property enhancement when used for FRCPs but also possible applications in electrochemical detection [73], structural batteries and energy storage [74], low power resistive heaters for advanced composite structures [75], and electromagnetic shield [76].

2.3 Spray deposition

A seemingly simple, yet technologically intensive technique used to transfer CNTs onto the fiber is the method of spray deposition. In this technique, dispersions of CNTs made with solvents and dispersants are sprayed directly onto fibers using a spraying device, as depicted in **Figure 3**. The technique allows CNT powders to be used, which is the most popular commercial form available. Although relatively simple in procedure, this technique does have its drawbacks. First, a homogeneous dispersion of CNTs must be prepared with time and resource-consuming techniques. The CNTs utilized must be carefully purified from the synthesis byproducts. To

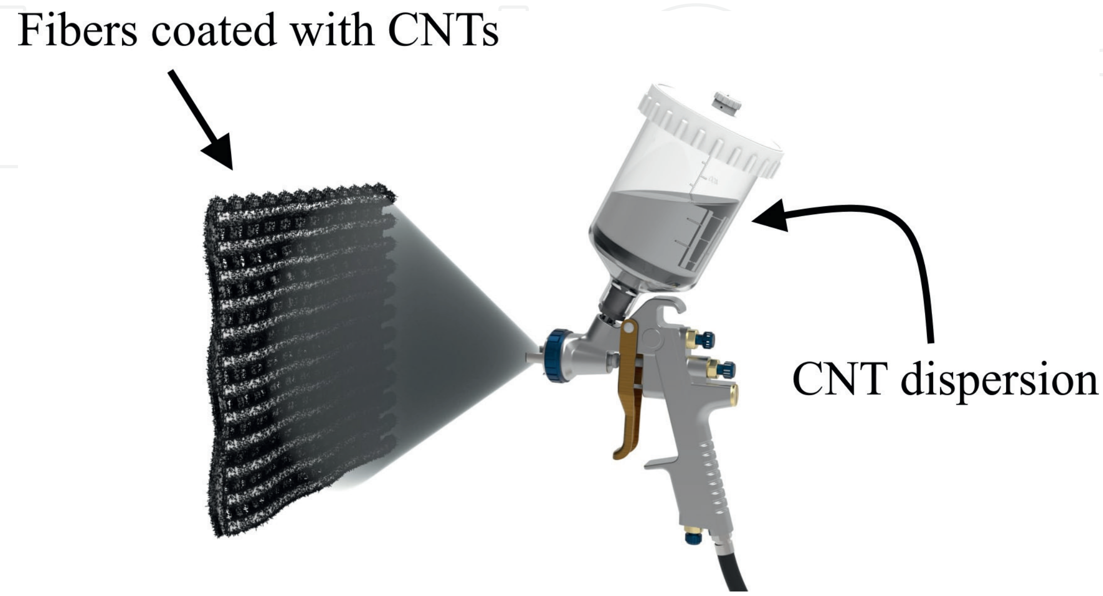

Figure 3.
Spray deposition of CNTs on fibers.

detangle CNT bundles usually mechanical mixers, ultrasonicators, high-speed homogenizers, or three-roll milling machines must be used. To avoid subsequent CNT agglomeration, surfactants are usually added in the dispersion. And finally, to get rid of large agglomerates, centrifugation techniques may also be necessary to apply. Then, to provide homogeneous dispersion on the surface of the fibers, the dwell time, spray rate, and coverage area all need to be monitored or planned. Further, to make sure that proper adhesion of the CNTs with the fibers takes place, the fibers themselves may need to be de-sized before the procedure. The solvents and dispersants that may be used in this technique also need to be checked for compatibility with the fibers and their sizing. Another major drawback of this technique is that the method randomly disperses CNTs on the fibers' surface, with alignment of the CNTs not being possible (without electrostatic modifications), which in turn makes the anisotropic properties of the end nanocomposite difficult to engineer.

Perry *et al.* showed that the spray deposition technique can be used to create laminar composites, which displayed Mode 1 fracture property increase (20%) with weight percentages as low as 0.057% [77]. Wang *et al.* showed that the process of deposition can be conducted using a simple commercial mechanical sprayer when coupled with a suitable dispersant [78]. The study showed that the flexural strength of natural FRPCs can be increased by up to ~38% and that the interfacial shear strength can be raised by ~25%. The study did, however, show that the deposition of the CNTs using this mechanical spray device was not as effective and uniform as other compressed gas-based spray devices. Lee *et al.* showed that by using a more efficient and standardized spray method, increases in tensile strength, modulus, and ultimate tensile strength were possible [79]. Li *et al.* dedicated a study to understanding the parameters that affect the final morphology and deposition degree of CNTs on fibers when the spraying technique is upgraded to electro-spraying [80]. The technique combines the traditional spraying technique with the application of voltage and electric connections, causing deposition to be aided by electrostatic forces. The study showed that with such modification to the process, the voltage is the main parameter dictating the deposition, especially when electrically conductive filaments such as carbon fiber are used. After voltage, it was found that the distance between the spray source and the deposition substrate (fibers) also influences the end morphology and deposition degree. The same electrodeposition technique was utilized by Sabri et al., where a 34% increase in fracture toughness was noted in samples with CNTs, the mechanism of toughening being attributed to fiber bridging [81]. Fogel *et al.* conducted a more systematic study where along with mechanical properties of the composites, the electrical properties were also determined [82]. The study showed that the electrical conductivity of the composites made from CNTs reached almost twice the value of reference samples, whereas DC spectroscopy methods showed this value to be two and a half times the value. Dynamic mechanical analysis showed no major changes in behavior for the polymer matrix, whereas slight decreases in mechanical properties such as interlaminar shear strength and fracture toughness were noted.

Cao *et al.* reported the electromagnetic shielding properties of composites produced from this method of integration [83]. The electromagnetic shielding efficiency for these composites was as high as 76% for weight percentages as low as ~0.5%. At various weight percentages studied in the article, tensile strength showed the highest increase of 4.1% at a loading of ~0.1% by weight, flexural modulus increased by 28.6% at a loading of ~0.3% by weight, elastic modulus showed an increase of 5.4% at ~0.1% weight loading, and flexural modulus showed an increase of 24.6% at ~0.3% by weight loading. Electrical conductivity was noted to increase by 68% at a loading of ~0.5%, with an SE value of 25.4 dBm/m. Holubowitch *et al.* described the electrochemical application of CNTs dispersed through the spray technique, although without any fibrous reinforcement phase [84]. The work showed that composites manufactured from this technique can be compared in performance to those that are currently used as scientific standards. Zhang *et al.* demonstrated that the application technique can be used to manufacture self-diagnostic materials capable of detecting damage through piezoresistive response even at extremely low CNT additions of ~0.01% weight [85]. Simultaneously, these composites showed a marked increase in fracture toughness and interlaminar shear strength. A similar work by Gonzales et al. showed that nanocomposites produced with this method displayed simultaneous marked increases in flexural strength, electrical conductivity, and interlaminar shear strength at weight percentages below 1.0%, with piezoresistive gauge factors for self-monitoring as high as 6.5 [86]. The materials were also noted to have good cyclic response without drift or major variation. Li *et al.* described hybrid nanocomposites manufactured through this method with enhanced electrical (increase by a factor of 4) and thermal conductivities (increase of seven times) [87]. Zakria *et al.* reported similar increases in mechanical and thermal conductivity via the same technique coupled with electrostatic assistance [88].

2.4 Dip coating

This technique for integrating CNTs in FRPCs is inherently simple yet requires a liquid medium for effective transfer, as shown in **Figure 4**. In this technique, CNTs are pre-dispersed in a liquid, which may consist of a polymer matrix, solvent, dispersant, or all of the mentioned chemicals. Once an effective dispersion is created, the fibers are soaked in the liquid dispersion, causing the CNTs in the dispersion to be transferred to the fibers. The fiber medium, after a certain soaking time, is removed from the container and dried to remove the unwanted chemical species, leaving

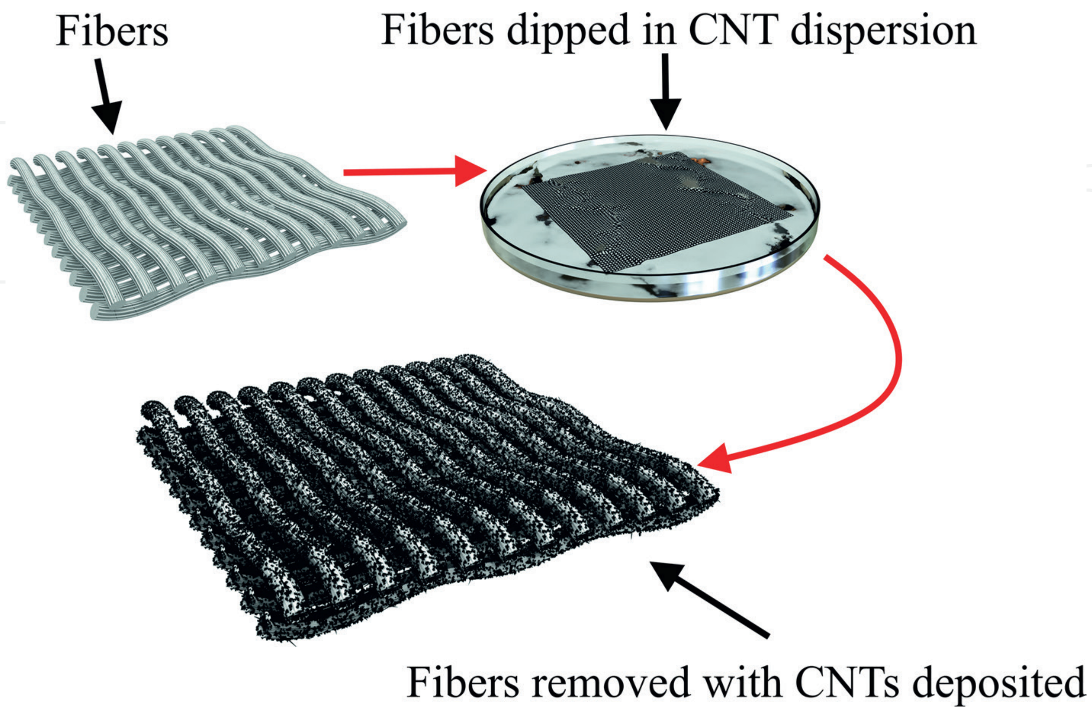

Figure 4.
Schematic representation of the dip coating technique.

behind the CNTs as a coating on the fibers. This technique, like spray coating, is also often coupled with electrostatic methods to ensure that effective and even transfer of CNTs to the fibers takes place.

Although this technique seems relatively simple, it is the method of integrating CNTs onto fibers that may result in the highest amount of variance. Firstly, to attain a dispersion of CNTs within a liquid requires processing machinery such as mechanical mixers, ultrasonicators, high-speed homogenizers, or three roll mills and extruders. Secondly, this solution needs to be optimized so that the dispersion is stable and agglomeration of the CNTs is minimized. In addition to the CNTs in the dispersion, the dispersants need to be carefully chosen so as to not cause any chemical or physical damage to the fibers being used. When soaking or transfer is taking place, this method provides no control as to how much or how many CNTs may be transferred onto a certain location of the fibrous reinforcement phase. Electrostatic techniques often help in this regard, controlling the amount of CNTs deposited on the fiber surface through voltage control. Finally, when inserting or removing the fibers from the dispersion used for coating, the movement and flow of the dispersion may cause an uneven amount of deposition, making the technique cumbersome and requiring a certain level or automation or delicacy.

Awan *et al.* showed than the dip coating method resulted in a better quality of CNT grafting and deposition than the aforementioned spray technique [89]. Rong *et al.* in their early publication showed that the technique may result in an increase of tensile strength from ~10 to ~25% [90]. Jamnani *et al.* reported that the technique of dip coating coupled with dispersants and chemical treatment resulted in an ultimate tensile strength increase of 38% and an interfacial shear strength increase of 116% at the optimum weight percentage and soaking time [91]. A work by Tzounis *et al.* focused on understanding the effect of chemical grafting and physical adsorption of CNTs on fibrous reinforcements and their end mechanical properties in the composites [92]. The study, which used dip coating to transfer CNTs from a solution to the intended fibrous reinforcement phase, showed that the composites produced with chemically bonded CNTs had lower electrical conductivities (~2 S/cm compared to 20 S/cm) and lower interfacial adhesion strength (48% lower than physically bonded CNT composites). Dip coating supported by electrophoretic deposition was shown to be feasible by Tamrakar *et al.* for controlling the thickness of the deposited CNTs (200 nm–2 μm [93]. The authors of the study showed that not only did the electrical conductivity of the composites increase, but the interfacial shear strength increase was as high as 58% compared with unmodified fibers. A similar study by Kwon *et al.* reported on hybrid nanofillers containing CNTs deposited on fibers using the electrophoretic deposition technique, which allowed increased interfacial adhesion of the fibers to the matrix, a ~10% increase in flexural strength, and simultaneously increased electrical conductivity of the final nanocomposite by ~1400% [94].

The multifunctional properties of FRCPs manufactured using this technique were described by Liu *et al.* [95]. The fibers produced during this study showed low electrical resistance at low weight percentages (~10^{-2} S/cm at 0.12–0.5% weight) while simultaneously showing major increases in tensile strength, Young's modulus, reduced Poisson ratio, and increased interfacial shear strength. Natural fiber-reinforced composites were manufactured and investigated using this manufacturing technique by Zhuang Liu *et al.* [96]. The study showed that even with natural fibers, electrical resistivity values may drop up to five magnitudes at low weight percentage addition of CNTs. The study showed that directional conductivity values were different along the path of the fibers and through the thickness of the composites.

The composites also showed sensitivity to thermal changes as thermistors, showing sensitivity to relative humidity as well as piezoresistive response with gauge factors of up to 12. One work by Liu *et al.* showed that by using this technique, simple cotton fabric can be functionalized and thus holds promise for applications in fiber-reinforced applications [97]. The work showed that simple cotton fabric can be made more mechanically stable, flame retardant, can be used as a UV blocking material not materials and be made superhydrophobic simultaneously, all with CNT loading percentages of less than 6%. A work by Lima *et al.*, in which a multifunctional cotton-doped CNT fiber was developed, showed that this technique was used to modify a fibrous structure and endow it with antibacterial and electrochemical performance, while being able to self-heat under the application of electricity [98]. The study showed potential applications of CNT/fiber composites for personal smart devices. Tzounis *et al.* showed similar multifunctional behavior of composites manufactured through the same method, where the final composites were electrically conductive (~10 S/cm), could be used for self-determining the degree of curing of the composite via piezoresistive response, were sensitive to UV radiation while at the same time could be used as a thermoelectric energy harvester due to the semiconductive nature of the CNTs used to produce the nanocomposite [99].

In addition, this versatile technique has been shown to be feasible for the production of transparent and flexible fiber-based electroluminescent devices [100], wearable electronics [101], and special fiber-based electrodes for human neuromodulators [102].

2.5 Dry transfer of CNTs

The last method described in this chapter is that of dry transfer. Probably the simplest method of integrating CNTs into fibrous reinforcement phases conceptually, dry transfer involves taking CNTs that have been collected on a substrate, bringing the CNT layer into contact with the intended fiber layer, applying a small amount of force to transfer the CNTs onto the fibers, and then removing the original collection substrate. This technique can be done both manually and with some degree of automation to make sure that the transfer is done efficiently. Since CNTs may be collected on a substrate randomly or in an aligned way during their synthesis, both types of CNT films have been investigated in literature for their use in manufacturing multifunctional nanocomposites. The basic dry transfer process has been schematically shown in **Figure 5** for randomly oriented films and **Figure 6** for aligned films.

Although seemingly simple, the technique does have its drawbacks. The application of force does not guarantee homogeneous removal of the CNTs from the collection substrate, often causing wrinkles and defects to appear in large-scale transfers. Furthermore, even when the application of force is uniform, since the receiving fibers are often woven, their surface is uneven and may cause defects in the film. CNT thin films themselves are delicate and easily break, which make the process extremely susceptible to damaging the films in one way or another. Another factor adding to the difficulty of this integration technique is that thin films often negatively impact the infusion capacity of the composites they are integrated in, especially when thick films are applied. Even though such drawbacks exist, many publications have shown that with proper process streamlining, the technique can produce large-scale multifunctional nanocomposites, as is seen in the following paragraphs of this section.

Randomly oriented CNT films have been shown to be feasible for integration into large-scale FRPCs while endowing them with multifunctional properties. Early

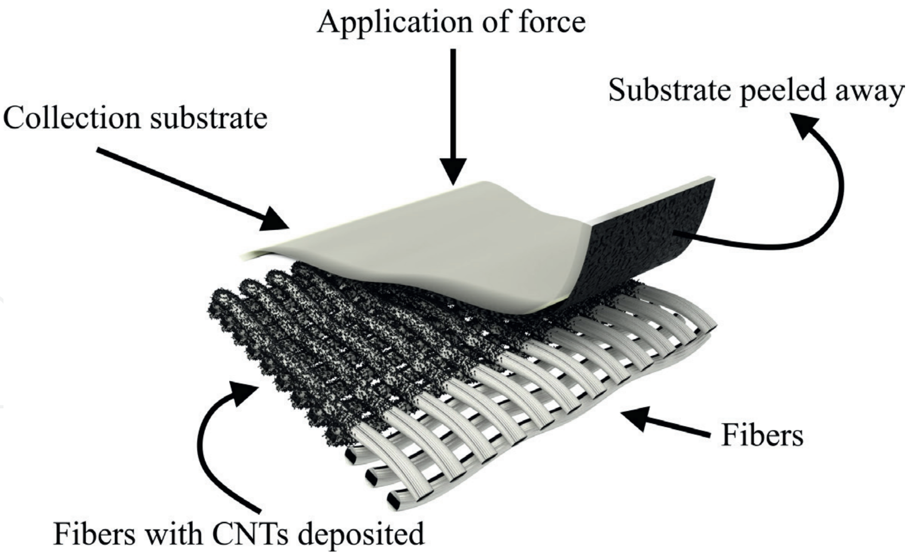

Figure 5.
Schematic showing the dry transfer technique for randomly oriented films.

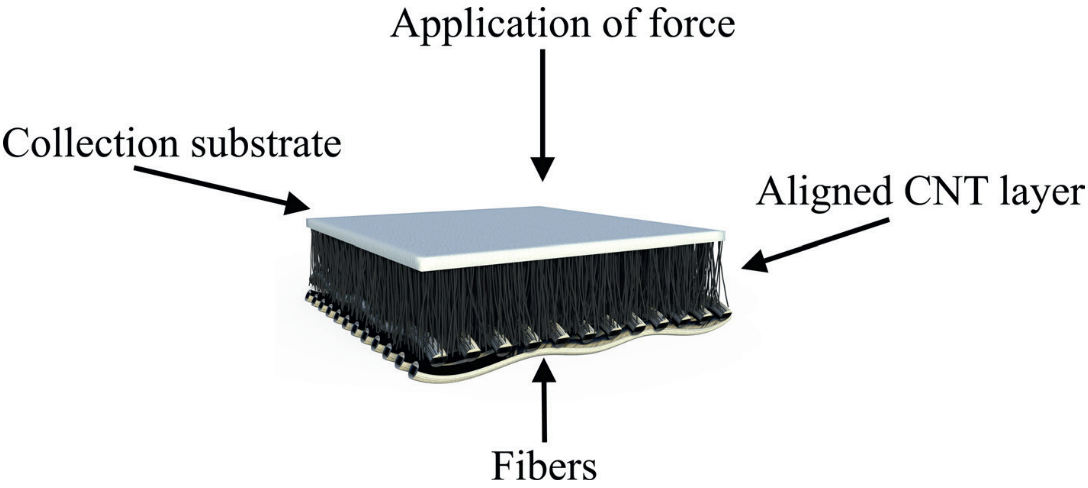

Figure 6.
Schematic showing the dry transfer technique for aligned films.

publications on the topic such as by Wang *et al.* [103], which used randomly oriented thin films as interplies for FRPCs, showed that their inclusion could cause an increase in tensile strength, tensile modulus and provide significant directional electrical conductivity. However, the work did highlight that the inclusion of such thin films may cause voids and defects, owing to the fact that resin infiltration in the large-scale composites may be negatively impacted.

Zhang *et al.* [104] reported on multifunctional composites made by the integration of CNT thin films, where the end composite could be used for the self-sensing of strain and damage, showing gauge factors between ~1.5 and 6 and that such material systems had a future in structural health monitoring. A similar work by Pan *et al.* successfully created ultrathin and flexible carbon fiber composites with CNT thin film interlayers [105]. The composites showed a good load transfer between the layers, reduced delamination, and improved interfacial bonding along with increased damping capability. A comparable tensile strength and tensile modulus to that of the unmodified composite were noted, with the electrical conductivity of the nanocomposite being 2 magnitudes higher. Li *et al.* studied in detail the effects of thickness of the films used for reinforcing FRPCs as well as the testing conditions used for interlaminar fracture toughness, with the results indicating that for quasistatic loading, two films applied together provided the best results whereas for Mode 1 fracture, the greater the number of films, the tougher the composite [106]. However, the work did show that increasing the number of layers did reduce the impregnation of the films by the matrix, leading to crack origination and propagation at the CNT interlayers.

While such interlayers have been investigated for their influence on mechanical properties, authors have also focused on their specific multifunctional property enhancement abilities. Ribeiro *et al.* showed that the incorporation of randomly oriented CNT thin films provided no major benefits to the composite in terms of interlaminar shear and compressive shear strength, yet managed to improve the thermal stability and glass transition temperature. The study also showed that such composites could provide electromagnetic shielding in the X-band region, with a ~ 99% attenuation rate [107]. The same author showed in a later publication that the electromagnetic shielding of such composites is frequency-dependent and can thus be tailored if needed [108]. Xu *et al.* showed that such thin films incorporated into composites can be used for resistive heating and curing of the composites themselves during manufacturing, with no major differences noted in the glass transition, curing degree, or tensile properties when compared with traditional oven curing [109]. The study also showed that such films can be incorporated into composites for the practical application of de-icing during the service conditions of typical composites. Lu *et al.* reported on the usage of CNT thin films for the manufacturing monitoring of FRPCs [110]. The authors described the different stages of polymer curing during the manufacturing process through piezoresistive changes, while the interlayer was also able to show sensitivity to the amount of solvents typically used during composite manufacturing. In addition, the work showed that the CNT thin film interlayer was also sensitive to temperature changes and showed a range of responses dependent upon the temperature range. In their work, Slobodian *et al.* presented results confirming the structural health monitoring ability of such composites to deformation, with gauge factors for pristine films being ~5, with an increase to ~500 when additional doping is applied [111]. Han *et al.* utilized composites incorporating CNT thin films for lightning strike protection [112]. The work, which combined electrical and non-destructive testing techniques, proved that for both visible and underlying damage of the composites, incorporation of an electrically conductive CNT film was essential to providing superior protection and post-strike mechanical properties. Li *et al.* reported on the flame-retardant properties of CNT thin films compounded with polyethersulfone, showing that the films help reduce the amount of heat released during combustion and help form a char, which helps to extinguish flames [113]. Hao *et al.* showed in their work that CNT interlayers can be combined with electrical impedance tomography to identify subsurface structural damage in composite materials [114].

Aligned CNT films are usually used as interlayers to maintain the alignment-dependent properties of the CNTs and provide direction or anisotropic properties to the composites they are integrated in. Garcia *et al.* utilized aligned CNT interlayers as joining surfaces between the layers of a FRPC [115]. The study showed that due to the interlayer integration, a 1.5–2.5 times increase in Mode 1 and three times increase in Mode 2 fracture toughness were seen. The aligned CNTs acted as reinforcing agents, which provided a crack bridging effect. The same author showed in another work that the interlaminar fracture toughness increased by 155% [116]. Ni *et al.* showed similar results in a recent work [117], where a so-called nanostitch layer of aligned CNTs was integrated in FRPCs without a change in final thickness. The work showed that the toughness of the CNT layer caused intralaminar fracture to take place as opposed to interlaminar. Villoria *et al.* from the same research group showed that the same interlayers may cause a 30% increase in tension-bearing critical strength, 14% increase in open-hole compression ultimate strength, and an increase in L-section bending energy and deflection by more than 25% [118]. Bhanushali *et al.* reported that by including aligned CNT films into composites as interlayers, the fracture toughness of the composites may increase by ~20–47% but only when interlayer thickness is low [119]. No changes in tensile behavior were reported in the study, but an increase in electrical conductivity was noted. Aly *et al.* showed in their work that the addition of aligned CNT films can increase the compressive strength of FRPCs [120]. In combination with this increase in compressive strength, structural health monitoring for damage could be conducted via the piezoresistive response and gauge factors of between 25 and 45 were reported. The publication showed that a smaller number of films, where the resistance is presumably higher, showed a greater overall piezoresistive response as compared with a large number of films. The response of the films was also asymmetric, with tensile loading leading to an increase in resistance while compression led to a decrease. This was confirmed in cyclic testing, where the cyclic piezoresistive response of the composites was also confirmed. Hallander *et al.* examined the mechanics of deformation of aligned CNT films in FRPCs and found that there was an increase in both intraply shear stiffness and interply friction when the film is used for composite manufacturing [121]. It was also found that the aligned film was more prone to shear than buckling when subjected to testing.

A number of researchers have identified fields and applications where the multifunctional properties of aligned CNT films may be exploited. Lee *et al*. proved that the electrical conductivity of such layers can be used for the heating and curing of composites without the need for an external autoclave or oven [122]. The work showed that no significant difference existed for composites made from internal heating of the CNT film embedded within the composite as compared with traditional autoclave or oven heating in terms of degree of cure, dynamic mechanical analysis, shear beam test, and double notch-based tensile testing. The technique, however, did show itself to be more energy-efficient [123]. The same author showed that such aligned CNT films can be used for the *in-situ* cure monitoring of thermoset matrices, often used to manufacture high-performance composites [68]. Work by Tarfaoui *et al*. exploited the self-heating characteristics of such films for the purpose of de-icing composite structures, showing low heating times with films as low as 60 μm in thickness [124]. Meng *et al*. demonstrated the combination of aligned CNT films along with glass fiber and Kevlar to produce structural composite batteries, which showed an energy density of ~1.4 Wh/kg, an elastic modulus of 7 GPa, and tensile strength exceeding 0.27 GPa [125]. Tensile testing showed stability of operation of the material during uniaxial loading and proved the feasibility of potential application. Aly *et al.* elaborated on the strain sensing ability of aligned CNT film integrated composites for the purpose of structural health monitoring in the interlaminar regions of FRPCs [126]. The study showed that no major difference in mechanical properties occurred with the inclusion of the aligned CNT films, gauge factors of up to 20 were seen during tensile testing, and that pre-straining the films caused a consecutive increase in sensitivity as cyclic testing progressed. The same author studied the structural health monitoring ability of FRPCs with aligned CNT films in three locations; in the middle of the composite and at the top and bottom most plies [127]. This study showed results pertaining to both monotonic and dynamic flexural loading, with gauge factors of ~6 being recorded. It was also shown that the film on the tension side of the samples showed a greater sensitivity to loading than the one on the compression side, while the layer in the middle showed greater sensitivity as the load increased. Conway *et al.* reported that the use of aligned CNT films can increase the impact resistance of carbon fiber-reinforced polymers, raising the residual strength by up to 16% [128]. A more exotic application was shown by Li [129], where in combination with carbon fiber sheets, aligned CNT films were shown to be remarkable electrode materials for potential applications in supercapacitors. Besides the low electrical resistance of the material, the electrodes showed good chemical and cyclic stability and strong resistance to water impact owing to the mechanical properties of the structure. In addition to the studies listed, aligned CNT films have been shown to have potential in applications such as the creation of CNT based macrostructures [130], dry electrochemical electrodes [131], composite pressure sensors [132], gas sensors [133], 3-D printing materials [134], thermal management materials [135], and a host of biology-related applications [136–140].

3. Conclusions

This book chapter aims to provide an overview for the techniques used to integrate CNTs into FRPC materials. The chapter overviews notable work regarding the main techniques and focuses on the published results by authors who have built both the foundations of the field and are currently working on the cutting edge of fiber-based integration techniques. The chapter touches upon the trends seen in mechanical properties attained by the various techniques discussed while combining the discussion with multifunctional properties such as electrical conductivity, electromagnetic shielding, flame retardancy, thermal conductivity and management, and sensors based on these materials.

Although a large amount of research work has been conducted on CNTs and their integration in FRPCs, the modern works clearly show that with new characterization techniques and application fields, an increasing number of doors for the practical application of such composites are opening, especially since the field of composites in general is shifting toward the large-scale integration of nanomaterials for smarter, stronger composite systems. Thus, CNTs and their application techniques and final properties of the end nanocomposites are a field that continues to grow and is expected to keep pace of growth for the forthcoming future.

In the near future, the authors see that CNT incorporating nanocomposites, which are hierarchical in nature, utilizing a combination of nanoparticles and multilevel reinforcements are going to become popular and the center of research attention. Combining CNTs with specialized high-performance fibers, shape memory matrices, self-healing nanoparticles, adaptive materials and making them from precursors and matrices which are biodegradable are avenues which the authors expect to be explored in the coming years. Such advanced materials will not only revolutionize the industry, but how we deal with composite lifecycle management and long-term usage.

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