Review Article

Jianbin Li, Zhifang Zhang*, Jiyang Fu*, Zhihong Liang, and Karthik Ram Ramakrishnan

Mechanical properties and structural health monitoring performance of carbon nanotube-modified FRP composites: A review

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Abstract: Fiber-reinforced polymer composites are high-performance materials used extensively in aerospace and defense industries. Researchers have added various nanoscale materials to FRPs for improving their mechanical properties and to prepare multifunctional composites. Carbon nanotubes (CNTs) with their high strength, high modulus, and large aspect ratio have emerged as a frontrunner in the nano-reinforcements, and there is a large volume of published research on this topic. This article provides an extensive review of key publications covering topics of fabrication methods, enhancement of mechanical properties, and applications of CNT-modified FRP materials in structural health monitoring. A description of the main methods of adding CNTs into FRP materials, including dispersion in the resin and film lay-up, is presented. A key focus of the review is the effect of CNTs on the mechanical properties of FRP composites, including interlaminar fracture toughness, impact resistance, and fatigue properties. Since CNTs have self-sensing properties, there is potential to use CNTs for nondestructive identification (NDI) and structural health monitoring (SHM) of composite structures. Finally, a discussion of the problems that might be encountered during the use of CNTs as nano-reinforcements in FRP, and the future application potential of CNT-modified FRP materials is reported.

Keywords: carbon nanotubes, multi-scale hybrid composites, fiber reinforced polymer, preparation of reinforced composites, impact and fracture properties, structural health monitoring, finite element modeling

Abbreviations

CFRP carbon fiber reinforced polymer composite
GFRP glass fiber reinforced polymer composite
CF carbon fibers
CNTs carbon nanotubes
SWCNTs single-walled carbon nanotubes
MWCNTs multi-walled carbon nanotubes
OMWCNTs oxidized multi-walled carbon nanotubes
CNT films carbon nanotube films
BPs bucky paper
DCB double cantilever beam test
ENF end notched flexure test
SBS short beam shear test
CST compression shear tests
OHT open hole tension
CVD chemical vapor deposition
EPD electrophoretic deposition
VARTM vacuum-assisted resin transfer molding
FCCVD floating catalyst chemical vapor deposition
GIC mode I interlaminar fracture toughness
GIIIC mode II interlaminar fracture toughness
ILSS interlaminar shear strength
RTM resin transfer molding
SEM scanning electron microscope
TEM transmission electron microscope
CZM cohesive zone modeling
VUMAT user subroutine to define material
NDI non-destructive identification
SHM structural health monitoring
1 Introduction

1.1 The superior performance of carbon nanotubes

Carbon nanotubes (CNTs) were discovered in 1991 by Japanese scientist Iijima [1] and have attracted huge attention among the research community due to their superior material properties. CNTs are one-dimensional nanomaterials with a radial dimension being nanometers and an axial dimension being micrometers. The density of CNTs is only 1/6–1/7 of steel, but the tensile strength can reach 50–200 GPa, which is about 100 times that of standard steel. The elastic modulus of CNTs can reach 1 TPa, which is equivalent to the elastic modulus of diamond and is about five times that of steel [2]. CNTs have a perfect hexagonal structure and can be divided into single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs). There are different microstructures of SWCNT corresponding to armchair, zigzag, and chiral arrangement of hexagons around the circumference (Figure 1).

Figure 2 shows a typical TEM image of MWCNT and shows that the length of CNTs ranges from few tens of nanometers to several micrometers long. A higher magnification image shows that the outer diameter is of the order of 10 nm. MWCNTs are less flexible and have more structural defects compared to SWCNTs. Figure 3 shows how SWCNTs change to form MWCNTs by rolling the concentric graphene sheets. It means that the choice of using SWCNTs and MWCNTs depends on the area of application. CNTs also have the extraordinary capability
of recovering to the original status after large deformation. The excellent performance of CNTs was reported to be caused by their uniqueness to the quasi-one-dimensional $sp^2$-bonded structure of the CNTs [3].

Various preparation methods have been developed to manufacture CNTs, such as the electric arc, laser ablation, and chemical vapor deposition (CVD) [5–7]. The electric arc method is a simple and fast method to mainly prepare SWCNTs, but it is not suitable for mass production, and the CNTs prepared by this method exhibited many defects like low yield strength and difficulty to purify. CNTs can be prepared by the CVD method under low temperature and normal pressure, and this method is easy to implement and of low cost. It is possible to manufacture large quantities of CNTs by CVD, and the number of walls, diameter, length, and orientation can be controlled during the growth process [8]. Owing to the special molecular structure and the super-strong bonding force between carbon atoms, CNTs perform better than all current fibers and are recognized as the future super fiber. Due to the excellent performance in various aspects such as electrical and heat conductivity, mechanics, and chemistry, the application of CNTs has involved electronic and electrical components, biomedicine products, composite materials, chemical sensors, and so on [9–14]. CNTs can play an important role in improving mechanical and tribological properties, electrical conductivity, and thermal conductivity of metal matrix composites [15,16] such as magnesium, aluminum, copper, nickel, titanium, and iron matrix nanocomposites [17–19]. As a reinforcement material for ceramic matrix composites (CMCs), CNTs also improve their toughness and enhance their plastic deformation ability [20–22]. CNT-reinforced FRP materials have also been widely used in many fields such as aerospace, automotive engineering, marine engineering, and sports equipment [23], and it is the focus of this article.

### 1.2 Carbon nanotube-reinforced composite material

CNTs have so far been applied to many fields, and CNT-reinforced composite materials [24–27] are an important application of CNTs. As reinforcement, CNTs can improve the original material in aspects of strength, rigidity, crack resistance, and wear resistance. In addition to improving the mechanical properties of CNT-modified composite materials, conductive properties and other functional properties make it very attractive in practical engineering. In recent years, with the development of many intelligent and new materials, CNTs, with their excellent strength and rigidity, can be used as high-quality reinforcements and significantly improve the bonding force between the layers of FRP. Therefore, it can be used to design multiscale demanding functional composite materials. This multiscale and multifunctional reinforced FRP material not only takes advantage of the excellent mechanical properties of CNTs but also retains the superior properties of traditional fiber reinforcements. Meanwhile, this material also adds the functions of nanomaterials (conductivity, sensing ability, and thermal resistivity) [28]. Therefore, the application of CNTs to FRP composite materials according to functional requirements to form a multiscale and multifunctional hybrid composite material has become one of the current research hotspots. In terms of mechanics, this material is suitable for complex load environments that require high interlayer bonding force of FRP materials, such as bird strikes and tool drops (impact load), cyclic rotation of wind turbine blades (fatigue load) [29], and so on. In addition, the lightweight and high-strength material can also effectively improve energy consumption efficiency in practical applications.

Ovali [30] confirmed that the wear resistance of glass/epoxy composites increased with the addition of MWCNTs at different concentrations (0.5, 1, and 2 wt%). The composites’ wear resistance mechanism is mainly related to the interfacial adhesion between matrix and fiber. Song et al. [31] used a chemical method to graft hydroxylated CNTs onto oxidized carbon fibers to improve polyimide’s mechanical and tribological properties as a matrix and prepare multiscale reinforced composites. Friction tests showed that the friction coefficient and the wear rate of CF-CNTs/PI composite decreased by 23.2 and 55.9%, respectively, compared with the control group. Roy et al. [32] used different functionalized CNTs to enhance the tensile strength of carbon/epoxy composites. Cheng et al. [13] introduced a CNT-based network into the aramid fiber-reinforced composites, which increased the interfacial strength and the compressive strength by 131 and 82%, respectively. Zhang et al. [33] sprayed CNT on the carbon fiber prepreg and have significantly improved the mode I interlaminar fracture toughness ($G_{IC}$) of CFRP laminates at a very low concentration (0.47 wt%).

In 2010, the Zyvex Technologies company launched a lightweight composite ship, the Piranha uncrewed surface vessel. In 2012, the Zyvex used nanocomposite materials to make the cabin doors and other closure components of another human-crewed long-range ship, LRV-17. The maximum speed of LRV-17 at sea can exceed 40 knots. It is up to 1,500 nautical miles, more than three times the range of ships of the same size [34]. Those ships
were manufactured by Zyvex using the Arovex® Prepreg, which is Zyvex’s high-level CNT-reinforced fiber prepreg. This material is a multiscale reinforced material made of CNTs, graphene, and FRP composite materials (Figure 4 shows the schematic diagram of this material), which has excellent performance, that is, flexural modulus, flexural modulus, and fracture toughness increased by 35, 26, and 194%, respectively. These superior capabilities from Arovex® Prepreg mean that it has greatly improved durability, better mechanical properties, lower failure chance, and better cost performance for custom products. The use of this material can significantly reduce the weight of the hull, for instance, the door, so that to keep full compatibility with existing parts and maintain the same level of strength as the standard aluminum product.

In recent years, researchers have used the relationship between the electrical resistance change and the stress and strain of CNT-reinforced FRP composites before and after damage to determine the damage’s location, size, and extent combined with different verification methods. Therefore, the addition of CNTs has a significant effect on discovering invisible damage in FRP materials and its health monitoring. This article mainly introduces three parts:

1. The preparation method of CNT-reinforced FRP composites
2. The effect of CNTs on the mechanical properties of FRP materials
3. The exploratory research on CNT-reinforced FRP materials in NDI and SHM.

2 Preparation of CNT-reinforced FRP composite

The manufacturing methods of traditional FRP composites range from reinforcement of matrix with UD fibers to stacking up of 2D fabrics. More recently, the increasing need for enhanced interlaminar performance of FRP materials has resulted in methods such as through-thickness reinforcements and 3D interlocked preforms to be developed (Figure 5). The introduction of CNTs is a challenge to the traditional interlaminar enhancement of FRPs structures, and its improvement on the performance of FRPs has been widely seen in recent years. There are many advanced technologies for introducing CNTs in the current study [35,36]. Figure 6 summarizes the different techniques used for adding CNTs to the FRPs. The CNTs are incorporated into raw materials by mixing them into the matrix or chemically modifying fibers before the fiber-reinforced and matrix phases were combined. After the prepreg of FRPs was prepared by combining the fiber-reinforced phase with the matrix phase, CNTs could be introduced by integrating with the prepreg or directly inserting CNT films between the prepreg layers of FRPs.

2.1 Dispersion in matrix

The earliest method of introducing CNTs to reinforce FRP materials is to directly disperse the CNTs in the resin matrix of FRP. After CNTs dispersed into the resin matrix, they can act as a bridge at the fiber–resin interface, which can effectively transfer stress, prevent crack propagation, and strengthen the interface and matrix. Therefore, CNTs can effectively improve the mechanical properties of the composite material. The dispersing techniques include mixing techniques with shear mixing; either mechanical or magnetic, calendaring, extrusion, ball milling, or ultrasonication (Figure 7 shows the schematic of dispersing techniques). Gupta et al. [37] used microfluidic processing (MF), planetary shear mixing (PSM), and ultrasonication (US)-dispersed MWCNTs in bisphenol F-based epoxy resin. The results showed that the MWCNTs were dispersed more homogeneous by MF and PSM processing yields than by PSM or US + PSM samples. Compared with the original epoxy resin, the tensile strength of the nanocomposites processed by this method is increased by 15%. Siddiqui et al. [38] manufactured prepregs of CFRP by dispersing the CNTs into the matrix based on the solventless prepreg process. The results confirmed that high-speed shear mixing and functionalization of CNT can effectively
Figure 5: FRP structure forms from 1D to 3D. (a) Typical preparation method of FRP laminates, (b) unidirectional structure, and (c) 2D woven fabrics. The reinforcement methods to improve the out-of-plane properties of FRPs: (d) 3D orthogonal preform, (e) 3D through-the-thickness preform, (f) 3D angle interlock preform, and (g) 3D orthogonal circular preform [36].

Figure 6: Different preparation methods of CNT-reinforced FRP.
lower the viscosity of the CNT-epoxy nanocomposites and thus can reduce the influence of excessive CNT content. Some of the dispersing methods' schematics are illustrated in Figure 8. However, one of the main challenges with these techniques is obtaining uniform dispersion of the CNTs in the matrix. At high volume fractions, CNTs can cause agglomerates that degrade the material properties. The high viscosity of the CNT-modified resin is also a limitation for certain manufacturing methods. Improving dispersion techniques, controlling the appropriate dispersion concentration of CNTs, and modifying CNTs can effectively reduce excessive viscosity.

2.2 Growth onto fiber

The second method is using CNTs to modify the reinforced fibers so that CNTs can directly grow onto the fiber. It is implemented mainly in three methods: chemical vapor deposition (CVD), electrophoretic deposition (EPD), and chemical grafting [39–43]. The CVD is a proven method for producing CNTs with high scalability, simple process, cost-effectiveness, and high quality. The CVD method achieves the growth of CNTs in fiber by circulating carbon precursors in the gas phase through a catalyst supported on a substrate [44–46]. Rong et al. [47] demonstrated that the chemical and CVD methods to grow CNTs onto fiber are efficient techniques for the uniform deposition of CNTs on the surface of carbon fiber. Compared with CF/epoxy materials, the tensile and flexural properties of multiscale reinforced materials prepared by these methods have been improved. Sager et al. [48] used the CVD method to prepare two different forms of reinforcements, namely, CNTs reinforcements formed by oriented growth and free growth. Results of the single-fiber fragmentation tests indicate an improvement in interfacial shear strength with the addition of a nanotube coating. Wang et al. [41] used the CVD process to prepare excellent CNTs/CF reinforced multiscale materials by adjusting the moving speed of carbon fibers and the ratio of catalysts in the growing atmosphere, which improved the structural and mechanical properties of the CF/epoxy.

The EPD method is also a powerful technique for incorporating CNTs such as CNT coatings and composite films with controlled architectures onto reinforcement fibers in the FRPs [49]. Figure 9 shows the schematic of the EPD method. Electrodes are placed vertically in the deposition cell containing a (here negatively) charged CNT suspension. Under the influence of an externally applied electric field, the charged CNTs migrate toward the electrode of the opposite charge (here anode) accumulating to form a coherent deposit. Of course, this method can also prepare separate films to strengthen FRPs. This method is a cost-effective method to manipulate CNTs for the ordered deposition of CNT coatings/films on the fiber surfaces, as well as for shaping the prepregs of targeted FRPs and finally obtain required performance such as mechanical properties between layers [42,50].
The method of chemical grafting is to graft CNTs to the surface of carbon fiber through chemical or physical bonds. Yongqiang and Chunzheng [51] grafted high-density CNTs onto carbon fibers using coupling agents that could provide more active groups, which were beneficial for grafting CNTs onto CF surface to prepare multiscale reinforcement materials. The results showed that the ILSS and impact toughness of the reinforced material were improved. Laachachi et al. [52] used this method to graft carboxyl and amino groups on CNTs and carbon fiber through acidification and heat treatment. The fiber washing and ultrasonic bath results shown that the grafting effect is better than the neat sample.

Despite the excellent preparation performance and diversified goals design, growing onto fiber still requires rigorously to design the process conditions, technical equipment, and operation modes. Hence, it is not suitable to carry out the mass production of CNT-reinforced FRP by using this method.

2.3 Prepreg modification

Compared with the aforementioned methods to add CNTs to the fiber or resin component of FRP, the third method is to disperse CNTs on the prepreg such as transfer printing [53,54], manual spreading, and spreading of CNTs powder. Santos et al. [55] sprayed the carbon chain length of two different amino-functionalized carbon nanotubes (commercial and laboratory growth CNTs) to the CF/epoxy prepregs. The experiment results confirmed that the introduction of CNTs contributed to the fragility properties of the prepregs. Rodriguez-González and Rubio-González [56,57] sprayed MWCNTs/ethanol solution through the ultrasonic bath during the fabrication in an autoclave (Figure 10 shows the schematic of spraying) to prepare different concentrations (0.05, 0.1, 0.2, and 0.5 wt%) carbon fiber/epoxy composite laminates with MWCNTs. Compared with control groups, the mixed-mode bending tests (MMB) showed the mixed-mode I/II interlaminar fracture toughness ($G_{IIC}$) of reinforced samples with 0.2 wt% MWCNTs were improved significantly. Mujika et al. [58] sprayed a solution containing MWCNTs on the surface of prepregs and prepared CNT-reinforced FRP composites by autoclave molding after the solvent volatilized. Experiments have confirmed that compared with the control group, a maximum increase of 22% in initiation fracture toughness and an increase of 14% in the propagation fracture
toughness were observed in the samples with functionalized CNTs. Williams et al. [59] uniformly dispersed the plasma-modified CNTs in ethanol to prepare a dispersion to coat the CNTs on the surface of the glass fiber prepreg evenly. By adding different areal densities of CNTs (0, 1.2, 1.6, and 2.0 g/m²) to strengthen the glass fiber-reinforced polymers (GFRPs), it shows that when the areal density is 1.6 g/m², the initiation and propagation of the fracture toughness increase up to 22 and 46%, respectively. Zhang et al. [33] dispersed CNTs in the formaldehyde solution by ultrasonic treatment to make CNTs uniformly mixed. Then, the prepreg was heated and cured at a constant temperature (Figure 11 shows the spraying process) to prepare a CFRP that contains low CNT density. The double cantilever beam (DCB) test confirmed that the \( G_{IC} \) of the reinforced laminates with a low CNT weight (0.02 and 0.047 wt%) was increased by 22 and 47%, respectively.

### 2.4 CNT film insertion

CNT film is a two-dimensional CNTs network structure formed by filling CNTs arrays freely on the film plane through physical or chemical methods. According to the orientation of the CNT array, CNT films can be divided into the horizontal, vertical, and mixed arrangement of CNT films. Now the methods of fabricating CNT films can be divided into two main categories: wet and dry methods [60], the most common methods are CNT solution filtration [61], drawing [62] or knocking down of CNT arrays [63], and directly synthesizing through floating catalyst chemical vapor deposition (FCCVD) [60,64]. Typical combination methods of CNT film and FRP prepreg is hand lay-up [65,66] (Figure 12 shows the processing). CNT films retain the original properties of CNTs and have the advantages of being highly porous; possess desirable mechanical, electrical, and thermal properties; and most importantly can be easily integrated into the existing composite material. Compared to CNT fibers and dispersed solutions, producing large-area CNT films with a low cost is much easier. So it is widely used in many fields [60]. CNT films are a two-dimensional macroscopic body with a self-supporting structure formed by entangled or interwoven CNTs. It is easier to form a hybrid reinforcement with FRP without losing the excellent properties of CNTs, and CNT films can be directly applied to the preparation of current FRP products without changing the process. Because of it, CNT films have excellent application prospects.

Shin and Kim [66] laid up bucky papers (BPs) in CFRP, which significantly improved the interlaminar fracture toughness. The CNT films were intercalated into CF prepregs to fabricate hybrid composites by using the FCCVD method. Zhouyi et al. [67] confirmed that the introduction of CNT films improved the compressive properties, interlaminar properties, and water resistance of CFRP. Deng et al. [68] manufactured CNT film-reinforced CFRP by inserting nonoriented and oriented CNT films into FRP for interlayer toughening to study the effects of the forming process, orientation, and surface density of

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**Figure 11:** Schematic illustration for the spray coating process [33].
CNTs on the mechanical properties and interlaminar toughness of composites. The results show that CNT films laid parallel to carbon fibers with small surface density have an excellent effect on improving composites' mechanical properties. Sanna et al. [69] manufactured nanocomposite films containing MWCNTs with higher conductivity by optimizing processing parameters and materials. At the same time, by further optimizing the type and concentration of surfactant used in the manufactured processing, CNTs were better dispersed to prepare nanocomposite films with higher conductivity. This film can be used in FRP materials that require high electrical conductivity, such as electromagnetic interference shielding.

In summary, the existing methods of adding CNTs to FRP are summarized. These methods have realized the incorporation of CNTs into FRP in terms of different dimensions by dispersing/grafting CNTs to FRP constituent materials, by adding CNTs to a two-dimensional FRP prepreg, or by inserting a CNT film into three-dimensional FRP laminates. The introduction of different CNT forms in FRPs provides more potential application for the lightweight construction of composite structures.

3 Mechanical properties of CNT-reinforced FRP

FRP composites have high in-plane tensile strength and rigidity but, due to its anisotropic characteristics, the compression resistance and interlayer performance are relatively poor. Generally, the damage mechanisms of FRP include matrix cracking, fiber breakage, and debonding/delamination. Among them, the composite delamination is a common form of damage. According to statistics, about 60% of the damage of composite materials is delamination damage in aircraft. Delamination can be caused by various loads received during the service of the composite structures, such as cyclic fatigue load, static bending, compression, tensile load, and impact load. Damage modes such as delamination will rapidly decrease the load-bearing capacity of the FRP laminate structure and may cause the failure of structures below the design load level. Therefore, it is essential to improve the interlayer performance of the FRP laminated structures. Researchers have shown that the adding density of CNTs has a significant improvement effect on the interlaminar fracture toughness, impact damage resistance, and fatigue performance of traditional FRP. In this section, the literature on the improvement of interlaminar fracture toughness, impact, and fatigue damage resistance after adding CNTs are summarized.

3.1 Interlaminar fracture toughness and interlaminar shear strength

Fracture toughness (FT), which mainly refers to the ability of composite materials to resist brittle fracture, is an indicator of the resistance to the fracture of materials. Brittle fracture is one of the most common types of structural failure [70]. Domun et al. [71,72] provided a comprehensive review of the improvement in modulus, tensile strength, and fracture toughness of brittle epoxy resins by the addition of nanoparticles. It was reported that a combination of CNT debonding and pull-out contributed to the toughening mechanisms in the highly crosslinked polymer and that the substantial increase in fracture toughness was achieved even at low filler content. There is also substantial literature on the improvement in interlaminar fracture properties of FRP that can be achieved by the addition of CNTs. The mechanical properties of FRP depend on the ability to resist fracture to various crack propagation modes. The mode I fracture toughness ($G_{IC}$) of the matrix is generally measured by the double-cantilever beam test (DCB), while the mode II fracture toughness ($G_{IIc}$) can be measured by the end notched flexure (ENF) test. Khaled et al. [73] improved the interlaminar fracture toughness of CFRP by spraying CNT solution between CFRP layers. Joshi and Dikshit [74] dispersed MWCNTs between CFRP layers to improve the delamination resistance ability of CFRP. Deng et al. [75,76] introduced functional group-modified MWCNTs to enhance the mechanical properties of CF/epoxy materials and analyzed the mechanism of functional group enhancement. From a microscale view, CNT-reinforced multiscale composites' fracture toughness increases due to the crack bridging and pull-out toughening mechanism by CNTs (as shown in Figure 13). The key factors include the arrangement and the length of the

![Figure 12: Stacking schematic of hybridization of BP and CF to manufacture reinforced material [65].](Image)
CNTs, as well as the type of functionalization of the surface of the CNTs [77]. The factors affecting the fracture toughness of CNT-enhanced FRP are summarized in Figure 14.

For those earlier methods about adding CNTs to fiber-reinforced composites to enhance interlayer performance, most of them are to disperse CNTs in epoxy resin directly. Shan et al. [79] sprayed a high-viscosity epoxy resin, the E20, to the composite prepregs after adding and anchoring CNTs on the fabric surface efficiently. By using this method, three composite specimen groups were fabricated using different CFRPs, including as-received, CNT-deposited with E20, and CNT-deposited without E20. Compared with control samples, the CFRP, which includes CNT-deposited with E20, improved the $G_{IC}$ of the modified material and the ILSS by 24 and 12%, respectively. Chaudhry et al. [80] added CNTs to the interlayer surface of the woven carbon fiber cloth, from 0 to 4.0 g/m², with every 0.5 g/m² as interval, and a total of nine groups were prepared. The samples’ measurement showed that $G_{IC}$ of the sample with a surface concentration of 1.0 g/m² has increased by 32% compared to the control group. However, when the surface concentration of CNTs added exceeds 1.0 g/m², CNTs have an adverse effect on the interlayer fracture toughness. Fan et al. [81] added the oxidized MWCNTs between GFRP layers to improve the ILSS performance of GFRP. Short beam shear (SBS) test and compression shear test (CST) were conducted on the manufactured components to characterize the influence of the process and the weight percentage of nanotubes on the ILSS. The results show that the fabricated composites with 0.5, 1, and 2 wt% OMWCNTs/epoxy resin composites have the ILSS increased by 9.7, 20.5, and 33.1%. Ashrafi et al. [82] prepared a modified CFRP concentration of 0.1 wt% functionalized SWCNTs to take an experiment and found that the addition of CNTs can increase $G_{IC}$ and $G_{IC}$ by 13 and 28%, respectively, compared to the neat group. Rawat and Singh [83] prepared reinforcement materials by adding different concentrations of MWCNTs (0, 0.5, and 0.75 wt%)
to symmetrical GFRP laminates. SBS test confirmed that the concentration of 0.5 wt% MWCNT can increase the ILSS and the bending strength by 13.66 and 44.22%, respectively. Khan et al. [84] prepared CNT/CFRP-reinforced materials with two growth strategies using the optimal CNT grafting strategy. The experimental results showed that these methods could significantly improve the flexural properties and mode-II fracture toughness of conventional CFRPs.

Although the introduction of CNTs improves the interlaminar properties of FRPs materials, CNTs must be controlled at appropriate concentrations. Too high CNTs concentration can cause CNT agglomeration and reduce the performance of reinforcement materials. Raﬁee and Sahraei [85] developed a multiscale modeling technique for estimating interlaminar fracture toughness of laminated composites containing CNTs. The length, agglomeration, wavy shape, and orientation of CNTs were considered in the random variables to conduct a complete stochastic multiscale modeling procedure. Finally, the comparison between the experiment study and the modeling procedure showed that the results were in good agreement with each other. Meanwhile, it also verified that the agglomeration of CNTs at high concentrations hinders the typical performance of CNTs.

In recent years, researchers have inserted CNT films as a layer into the composite structure for toughening. Shin and Kim [66] studied the mode I and II interlaminar fracture toughness of BP/CFRP materials by DCB and ENF tests, respectively. The experimental results showed that the shear strength of BP/CFRP materials decreased slightly compared with the control group, but the $G_{\text{IC}}$ increased by 45.9%. Yu et al. [86] used the vacuum-assisted resin transfer molding (VARTM) to prepare CNT film-reinforced CFRP laminates to understand the effect of CNT films with different areal densities on the $G_{\text{IC}}$ of laminates. The experimental results show that as the surface density of the CNT films increases, the $G_{\text{IC}}$ gradually increases. When the areal density of the CNT films is 9.64 g/m$^2$, the $G_{\text{IC}}$ enhancement effect is the best, which has increased by 94% compared with the control group. Deng et al. [68] studied the effects of the CNT films molding process, orientation, and areal density on the mechanical properties of composite materials. They used spraying methods to prepare CNT film-reinforced materials with nondirections and film-drawing methods to prepare CNT film-reinforced materials with particular directions. Compression, bending, interlaminar shear, and interlaminar fracture toughness tests showed that the performance of CNT film-reinforced materials is related to the laying direction and surface density of CNT films. The smaller was the surface density, the better the toughening effect was. Under the same surface density, the interlaminar fracture toughness of the spraying method was higher than that of the CVD film-drawing method. When CNT films were parallel to carbon fibers, the compressive strength, 90° bending strength, and laminate shear strength of the composites were better than those in the vertical direction. Figure 15 shows the fracture morphology before and after adding CNTs random film to improve $G_{\text{IC}}$. When the surface density of the unoriented CNT films is 0.75 g/m$^2$ (as shown in Figure 16), the $G_{\text{IC}}$ and $G_{\text{IC}}$ of the material have the best enhancement after adding CNT films, which is increased by 21 and 42%, respectively. Xu et al. [87] improved the interlaminar shear strength of CFRP materials by controlling the number of layers laid by inserting continuous interlacing CNT films between CFRP layers. Finally, it was demonstrated that the ILSS of the reinforced CFRP with 0.22 wt% CNT films increased by 21.54% and the interlaced CNT films also dramatically improved the electrical conductivity of the laminates.

Zhouyi et al. [67] have studied the $G_{\text{IC}}$ of CNT film-reinforced CFRP material, and the results show that the $G_{\text{IC}}$ of the material is about 60% higher than the unmodified material. The scanning electron microscope (SEM) image showed that the bridging effect of the CNTs on the matrix leads to toughening. Liu et al. [88] prepared CNT film-reinforced CFRP material by using liquid molding resin transfer molding process, of which the $G_{\text{IC}}$ has increased from 1,292 J/m$^2$ of the control material to 2,869 J/m$^2$. With the improvement of the method, the mechanism of the CNT enhancement effect has gradually become clear, that is, the addition of CNTs to FRPs results in the substantial improvement in the mechanical properties of FRP.

In addition to adding conventional CNTs, there is also research about functionalized CNTs and other derivative materials added into FRP for enhancement. Borowski et al. [89] added CFRP with four different concentrations of carboxylate modified MWCNTs (COOH-MWCNTs) for the DCB test. The results show that the maximum $G_{\text{IC}}$ value of CFRP increased by 25, 20, and 17% after adding COOH-MWCNTs at 0.5, 1.0, and 1.5 wt% concentrations, respectively. The SEM image shows (as shown in Figure 17) that the new material forms a new energy dissipation mechanism. That is, a new crack extension branch is generated, which has increased the energy consumption of the material. Davis and Whelan [90] used fluorinated CNTs (f-CNTs) sprayed to prepare reinforced composites tested by the four-point end notch flexure test to measure $G_{\text{IC}}$ in the middle of the laminate ply. Compared with the neat group, the resistance to ILSS
of the reinforced material containing 0.5 wt% f-CNT has significantly improved. Liu and Yang [91] prepared MWCNTs grids with different thicknesses and inserted them into the interface of CFRP laminates. The end notch flexure test showed that the porous MWCNTs grid with a thickness of about 20 μm increased the \( G_{IC} \) and ILSS of the composite by about 69 and 24%, respectively. The failure mechanism analysis showed that the interaction between the modified functional groups and the epoxy promoted the formation of the strengthened

![Figure 15: Fracture morphology of CFRP laminates before and after adding CNTs random film: (1) the \( G_{IC} \) morphology of sample with (b) and without (a) unorientation CNT films; (2) the \( G_{IC} \) morphology of sample with (d) and without (c) unorientation CNT films [69].](image)

![Figure 16: CNTs random film surface density to increase the rate of \( G_{IC} \) and \( G_{IC} \). Data from ref. [68].](image)

![Figure 17: The SEM image shows that the MWCNTs in the sample containing 1.5 wt% COOH-MWCNTs are distributed in the epoxy resin matrix [90].](image)
interface between CF/CNTs and the resin [92], which changed the fracture mechanism of the composites and allowing the composites to withstand greater loads. Abidin et al. [93] proposed a new method of mixing pure epoxy solid powder and CNTs powder, which was then used to make FRP composites to improving the toughening potential of epoxy matrix by the distributed CNTs in the composite matrix. Compared with the control material and the CNT–FRP with the same content of CNTs, the experiment showed the $G_{IC}$ of these heterogeneous layup materials increased by 41 and 26%, respectively. Table 1 briefly summarizes the aforementioned research on the interlaminar properties ($G_{IC}$, $G_{IIC}$, and ILSS) of CNT-reinforced FRP.

### 3.2 Impact damage resistance

The impact is a common type of load in the application of composite structures. According to the speed and the resultant damage of impact, it is divided into low, medium, and high-speed impacts. Bullet impact is a typical example of high-speed and high-energy impact. This type of impact can produce extreme lateral deflection and partial perforation in a short time [96], which is visible and detectable by the naked eye. The aircraft encounters medium- and low-speed impacts such as bird strikes, hail strikes, or tool dropping during maintenance, which will cause invisible internal damage. According to the previous report, nearly 13% of maintenance records for damaged Boeing 747 aircraft were caused by foreign objects [97]. Radomes, radar antennas, windshields, nacelles, hatches, propeller blades, and even fuel tanks are all targets for in-flight strikes. Although high-performance composite materials have been widely used in aerospace, the aforementioned problems are still the focus of research today. This is due to the limited ability to absorb impact loads’ energy, the plasticity is poor, the interface is relatively weak, and the performance of composite laminates will be significantly reduced after impact [98]. Figure 18 shows the schematic of different kinds of damage mechanisms in three impact load.

It has been reported that the failure of composite structures when subjected to impact was caused by the destruction of a series of complex energy absorption mechanisms. Under impact loading, the complete failure process goes through the following stages [97,99]:

1. The initial failure caused by matrix cracking, fiber/matrix debonding, and transverse bending cracks in the bottom layer.

2. The formation and extension of cracks in the middle of the interface lead to the stratification between layers, resulting in further damage.

3. The fiber is damaged under tensile and slightly flexed under compression, which eventually leads to complete failure of the material.

The impact under low energy usually does not evolve to the mode of fiber failure, but at this time, interlaminar damage before fiber and resin has been generated in the interior of the material. Materials that undergo low energy impact do not cause significant damage, but these undetected damages are usually fatal, which is the focus of this section.

After the low energy impact, damage occurs inside the structures and the mechanical properties such as in-plane strength and stiffness are substantially degraded. So the mechanical properties of fiber and matrix, including matrix’s fracture toughness, interface properties, and fiber configuration play an essential role in determining the impact damage resistance and damage tolerance of composites [100,101].

The key point to improve the impact resistance of laminated structures is that the elastic behavior of the structures absorbs the impact energy [102]. Currently, the impact resistance can be improved by using high-strength fiber, improving fiber structure, optimizing matrix structure, and toughening the interface layer. CNTs are a reinforcing material that can improve the different systems of the lamination structure. The impact resistance property of composites can be significantly improved in CNT-modified FRPs, manifested in reducing the area of delamination damage after impact, and manifested in improving the compressive strength and damage tolerance of samples after impact.

Kostopoulos et al. [103] prepared an enhanced CFRP with the concentration of 0.5 wt% MWCNTs. Under the impact test at a range of energy levels, the impact performance, compression strength, and compression fatigue performance of the reinforced material can be improved. Wang et al. [104] studied the impact properties of pre-stretched GFRP materials modified by MWCNTs (0, 0.4, and 0.75 wt%). The experiment showed that the modified specimens reduced the damage and enhanced the perforation threshold under three impact energies (9, 16, and 22 J). The microscopic fractures indicated that the fracture, pull-out, and bridging of CNTs provided additional energy consumption mechanisms to prevent crack propagation (Figure 19 shows the failure modes).

Singh et al. [105] used 94.14 J impact energy and 6 m/s impact velocity on CFRP laminates with matrix, which has
| Resin/matrix | Type of CNTs/ concentrations | Preparation method | Experimental methods/ standard | Enhanced performance | Reference |
|-------------|-----------------------------|--------------------|---------------------------------|----------------------|-----------|
| GFRP/epoxy  | OMWCNTs 0.5/1/2 wt%         | Dispersed into resin/laminate curing | Compression shear tests (CST)/ ASTM D2344 | 9.7, 20.5, and 33.1% increase in ILSS of 0.5, 1, and 2 wt% contains, respectively | Fan et al. [81] (2008) |
| CFRP/epoxy  | SWCNTs 0.1 wt%              | Dispersed into resin/laminate curing | Double Cantilever beam (DCB) test/ ASTM D5528 13% increase in G\textsubscript{IC} (0.1 wt% SWCNTs) | Fan et al. [81] (2008) |
| CFRP/epoxy  | f-CNTs                      | Spraying/laminate curing | End notched flexure (ENF) test / ASTM D5528 28% increase in G\textsubscript{IC} (0.1 wt% SWCNTs) | Ashrafi et al. [82] (2011) |
| CFRP/epoxy  | COOH-MWCNTs                 | Surface spraying of prepreg | Four-point end notch flexure test | 23% (initial) and 27% (extended) increase in G\textsubscript{IC} | Davis and Whelan [90] (2011) |
| CFRP/epoxy  | CNTs 0.02/0.047 wt%         | Surface spraying of prepreg | DCB test/ ASTM D5528 | 24% (0.02 wt%) and 47% (0.047 wt%) increase in G\textsubscript{IC} | Shan et al. [79] (2013) |
| CFRP/epoxy  | CNT films                    | Two methods to prepare CNT films/laminate curing | JCB773-1996 (Chinese standard) 15.6% increase in ILSS (surface density: 3.8 g/m\textsuperscript{2}) | Deng et al. [68] (2015) |
| CFRP/epoxy  | CNT films                    | RTM process | G\textsubscript{IC}; HB 7402-1996 (Chinese standard) 24% increase in ILSS | Liu et al. [88] (2013) |
| CFRP/epoxy  | COOH-MWCNTs 0.5/1/3 wt%     | Dispersed into resin/laminate curing | DCB test/ ASTM D5528 41% increase in ILSS | Borowski et al. [89] (2015) |
| CFRP/epoxy  | COOH-MWCNTs                 | Preparation of MWCNT grid/laminate curing | ENF test/ ASTM D6671M-06 69% increase in G\textsubscript{IC} | Liu and Yang [91] (2015) |
| CFRP/epoxy  | MWCNTs                      | Dispersed into resin/laminate curing | ILSS: ASTM D2344 24% increase in ILSS | Rawat and Singh [83] (2016) |
| CFRP/epoxy  | CNT films                    | Depositing on CF/laminate curing | SBS test/ ASTM D2344 13.66% increase in ILSS | Chaudhry et al. [80] (2017) |
| CFRP/epoxy  | CNT films                    | Manual layup/laminate curing | ENF test/ ASTM D7905 32% increase in fracture toughness (1.0 g/m\textsuperscript{2}) | Zhouyi et al. [67] (2019) |
| CFRP/epoxy  | CNTs                         | Manual layup/VARTM | SBS test/ ASTM D2344 32% increase in fracture toughness (1.0 g/m\textsuperscript{2}) | Yu et al. [86] (2019) |
| CFRP/epoxy  | CNTs                         | NC powder prepared by CNTs and epoxy resin | DCB test/ ASTM D5528 41% (CNT reinforced) and 26% (control) increase in G\textsubscript{IC} | Abidin et al. [93] (2019) |

(Continued)
Table 1: Continued

| Resin/matrix | Type of CNTs/ concentrations | Preparation method | Experimental methods/ standard | Enhanced performance | Reference |
|--------------|------------------------------|--------------------|-------------------------------|---------------------|-----------|
| CFRP/epoxy   | CNTs                         | Grafting on CF/laminate curing | SBS test/ASTM D2344 SBS test/ISO-14130 Mode-II FT test/ASTM D3039 ENF test | ILSS improved 32% (type 1) and 105% (type 2) increase in ILSS 53% increase in $G_{IC}$ 53% increase in $G_{IC}$ | Khan et al. [84] (2019) |
| CFRP/epoxy   | Bucky paper                  | Lay-up/laminate curing    | SBS test/ISO 14130 32% increase in ILSS Shrin et al. [85] (2020) |                       |           |
| Epoxy        | CNTs                         | Dispersing into matrix    | Mode-I FT test/ASTM D5045 DBC test/ASTM D5528 | Fracture toughness improved Fracture toughness energy improved | Shin and Kim [66] (2021) Ma et al. [94] (2021) Rafiee and Sahraei [85] (2020) Yao et al. [95] (2020) |
| GFRP/epoxy   | MWCNTs                       | Dispersing into matrix/laminate curing | SBS test/ASTM D5528 |                       |           |
| CFRP/epoxy   | CNTs/functionized CNTs (oxygen) | Grafting on CF          | SBS test/IC/T 773-2010 (Chinese standard) | 13.78% (long and sparse) and 23.93% (short and dense) improve in ILSS (oxygen containing) |           |
Figure 18: Schematic showing different damage mechanisms due to impact load: (a) high energy, (b) medium energy, and (c) low energy [97].

Figure 19: Microscope failure mechanisms of 0.75% MWCNT-modified GFRPs under 22 J impact, (a) glass fiber bridging and debonding, (b) matrix cracks, and (c)–(e) CNT failure modes.
the impact of the different rates (3, 7, and 12 m/s) by the same experiment device [110,111], CFRP with different concentrations of CNT films (0, 1, 2, and 4 wt%) randomly distributed in epoxy resin was tested using a high-speed camera to record the sample deformation and damage propagation during impact. The results showed that the impact resistance of the reinforced material under high-speed was increased by 15.6% (7 m/s) compared to the control group (as shown in Figure 20). With the increase of CNTs (maximum concentration 4 wt%), the impact resistance improvement was more significant.

Xin et al. [112] confirmed that the adding amount of CNT films sheets could enhance the interlayer impact resistance of FRP. Under low-velocity impact, although the flexural performance of the reinforced material was slightly lower than the control group, it can significantly reduce the delamination area under low-velocity impact under the same impact energy (as shown in Figure 21). This research preliminarily proved that the CNT films have the potential of designing reinforced composite materials with additional functions and its cost in industrial production was lower than traditional preparation methods, and thus it had great potential for future development.

There are also researchers studying the medium- and high-speed impact properties of CNT-enhanced materials. Tehrani et al. [113] conducted a medium-speed impact test on the CFRP composite with MWCNTs and studied the impact resistance. The results showed that the introduction of MWCNTs could increase the impact energy absorption by 21%. This was due to the adhesion between the CNTs and matrix to enhance the interface property between matrix and fiber. Chihi et al. [114] used the Split Hopkinson pressure bar (SHPB) test device to analyze the mechanical properties of CNT-reinforced composites under different dynamic impact loads. The results showed that the introduction of different CNTs concentrations (0, 0.5, and 2 wt%) improved the failure mechanism of CFRP, increased its mechanical properties under dynamic loads, and reduced interlayer crack propagation and delamination.

In addition to the aforementioned research, Sharma and Lakkad [115] used CVD technology to grow MWCNTs on the surface of carbon fibers to prepare multiscale composites. The Charpy and the Izod impact test showed that the impact energy absorption of the reinforced material was increased by 48.7 and 42.2%, respectfully, compared
with the control group. The analysis of the impact samples’ fracture morphology showed that the presence of CNTs provided a bridging effect for microcracks and could improve the energy of impact absorption.

There is also literature on the effect of functional CNTs on the impact response of FRP. Soliman et al. [116] conducted five-level energy (15, 24, 30, 60, and 120 J) low-velocity impact on CFRP materials added with different concentrations (0.5, 1.0, and 1.5 wt%) of COOH-MWCNTs. The experimental results showed that the impact energy absorption of the 1.5 wt% functionalized MWCNT-reinforced FRP was increased by 50% compared to the control group.

Table 2 briefly summarizes the aforementioned reports about the impact resistance of the multiscale composites of CNT-reinforced FRP.

The aforementioned works have confirmed that the introduction of CNTs has a significant effect on improving the impact resistance of FRP. It can endow reinforced materials with higher damage tolerance and significantly impact on the multifunctional FRP materials. However, the current research still has a long way to go before practical application. One of the biggest challenges is the uneven dispersion and agglomeration of CNTs, which will inhibit the performance improvement of reinforced materials, such as the decline of Young's modulus, Poisson's ratio, and stiffness [117–119].

Currently, the effective suppression method is the use of functionalized CNT-enhanced homogeneous mixing method and bucky paper [120]. With the emergence of new methods such as CNT films enhancement, it has a great possibility to enhance properties of advanced materials in the application, which urgently need to improve special properties. From the research results of Xin et al. [112], the use of CNT films for enhancement has great potential for enhancing the interlayer performance of FRP, especially for the impact performance. The most important thing is that this method is more straightforward to commercialize than the traditional CNT dispersion method so that the CNT-enhanced FRP material can move from the laboratory to the batch production in the factory.

### 3.3 Fatigue resistance

FRP is widely used in many industries, especially wind power generation [121], which have a high requirement in fatigue resistance of the structural materials. So to improve the fatigue performance of FRP materials has become a research hotspot to explore [122]. From manufacturing to operation and maintenance, FRPs face fatigue loading conditions frequently. Due to its anisotropy and inhomogeneous nature, the strain development of FRP along the fiber direction is inconsistent with other directions, which is easy to initiate fatigue damage under vibration and other fluctuating loads [123,124]. In the early 1950s, due to successive disasters caused by fatigue of the Comet jet, the fatigue life and crack growth of the aircraft structures had attracted the attention of aircraft designers. During the fatigue process, the composite will experience a series of changes such as fiber fracture, fiber–matrix debonding, matrix cracking, and final failure. Crack failure due to fatigue load will undergo a process from initiation to propagation. Therefore, the fiber, the matrix, and the interface between matrix and fiber play an essential role in the fatigue performance of composites [124,125].

Because of its low cost and wide range of applications, GFRP was an early target for studying the fatigue properties. Grimmer and Dharan [126] conducted tension–tension fatigue tests on the GFRP with 1 wt% MWCNTs at 70, 60, 45, and 30% of the ultimate stress. The results showed that the high-cycle fatigue strength of the reinforced material was increased by 60–250% compared to the control group. The microscopic observation showed that the CNT fracture and pull-out were caused. It showed that the addition of CNTs had great potential for increased fatigue life, and it had also been confirmed in other researches [126–128]. Nevertheless, the addition of too much amount of nanoparticles would cause the fatigue life to decrease [26,128]. Böger et al. [129] showed that MWCNT-enhanced GFRP had a 16% increase in fracture strength through static tensile and dynamic fatigue tests, and the number of high-cycle fatigue life has increased by several orders in magnitude. The aforementioned results indicate that the increase in breaking strength between fibers may be related to the improvement in fatigue resistance for CNT-modified FRP.

As the high-strength properties of carbon fiber are recognized and the production cost is reduced, CFRP has been used more frequently in crucial engineering fields such as aerospace. More importantly, carbon fiber has a higher modulus of elasticity and stronger corrosion resistance than glass fiber [130], which leads to better resistance to axial high-cycle fatigue loads than GFRP under the same conditions. Currently, there are not much researches on studying the fatigue behavior after adding CNTs in CFRP structures. After adding 0.3 wt% of MWCNTs in the matrix, no effect was seen on the quasi-static properties of CFRP, but its fatigue life was improved [131]. SEM
| Ratio/ matrix | Type of CNTs/concentration | Experimental method/standard test | Enhanced performance |
|---------------|---------------------------|-----------------------------------|----------------------|
| CNTs/epoxy    | MWCNTs/0.5/1/1.5 wt%      | Drop weight impact test (energy level: 2, 6, 12, 16, 20 J, ASTM D5628) | The impact performance is improved in 12, 16, and 20 J. | Kostopoulos et al. [103] (2010) |
| CFPR/epoxy    | MWCNTs/0.4/0.75 wt%       | Intermediate velocity impact test/ASTM D790 | 12% increase in impact absorption energy | Soliman et al. [116] (2012) |
| CFPR/epoxy    | MWCNTs/0.5/1/2 wt%        | Low-velocity impact test (energy level: 0.5, 1.0 J) | 21% increase in impact absorption energy. | Tehrani et al. [113] (2013) |
| CFPR/epoxy    | MWCNTs/0.5/1/2 wt%        | High-speed impact test (using SHPB, stress: 1.4, 1.6, 1.8, and 2 bar) | 93% increase in the impact resistance of the MWCNT-reinforced Composite. | Rawat et al. [108] (2020) |
| CFPR/epoxy    | MWCNTs/0.5/2 wt%          | Compression after impact (CAI) test/ASTM D7136 | The best impact performance of the composite materials is better than the neat group and significantly reduces the delamination area. | Chihi et al. [114] (2020) |
| GFRP/epoxy    | MWCNTs/0.1/0.25/0.5/1.5 wt% | Drop weight impact test (energy level: 5, 6.6, 7.2, 8.5 J) | 91% increase in the impact resistance of the MWCNT-anchored CFRP. | Rawat et al. [109] (2020) |
observed that as the fatigue loading level increases, the energy absorption of the reinforced material and the damage mechanism changed from the macro-scale to the multiscale damage. Boroujeni and Al-Haik [127] used different growth methods to graft MWCNTs on CFRP and performed uniaxial tensile fatigue tests. Experimental results showed that the fatigue life of the reinforced material was increased by 150%. The fracture morphology of SEM showed that MWCNTs were protecting the fiber from matrix cracks, so the addition of MWCNTs can significantly improve the fatigue life. Currently, there are limited studies on the evaluation of the fatigue life of CNT-enhanced FRP. Most are still trying to improve the fatigue resistance of FRP composites by taking advantage of the excellent properties of CNTs, and few have explored the fatigue life prediction of CNT–FRP materials.

### 3.4 Simulation of CNT-enhanced FRP

The damage mechanisms of FRP composites are diverse and complex, resulting in the dispersion of the experimental tests. The simulation modeling is an alternative way for studying the damage of FRP and CNT-FRP. The computational simulation could be conducted to compare or expand the experimental results by simulating the uncompleted parts in the experiment. The numerical modeling of CNT-modified composite is possible at different scales ranging from atomistic modeling using molecular dynamics (MD) simulation to macroscopic modeling with homogenized properties. Gogoi et al. [132] used MD to tailor the surface chemistry of CF for an efficient and strong interphase with matrix and found that the presence of both CNT coating and surface functionalization of CF increases the IFSS values of the composite. The research methods of CNT-reinforced FRP materials will be diversified at different scales. Table 3 briefly summarizes the simulation-related research of multiscale CNT-reinforced FRP composites.

Currently, plenty of work has reported the simulation of damage for CNT-enhanced FRP. Pashmforoush [135] used ABAQUS/EXPLICIT to study a variety of damage modes in CNT-reinforced CFRP materials under the low-velocity impact, including matrix cracking, fiber damage predicted by the Hashin’s criterion, and delamination predicted by the cohesive zone modeling (CZM). Meanwhile, the experiments were carried out to validate the numerical results. Through FEM, the enhancement effect for

| Objects/test methods | Simulation method | Simulation result | Reference |
|----------------------|------------------|------------------|----------|
| Laminated beam with hole/tensile test | Software: ABAQUS/EXPLICIT | (1) The CZM accurately predicts damage expansion and delamination | Tarfaoui et al. [133,134] (2017) |
| CFRP plate/drop-weight impact test | Failure criteria: Hashin’s criterion | (1) The introduction of CNTs can reduce damage of impact | Pashmforoush [135] (2020) |
| CFRP plate/Taylor impact test | Software: ABAQUS/EXPLICIT | After introducing CNTs, the absorption of impact energy is improved, and the damage of the material is reduced | El Moumen et al. [111] (2018) |
| Square laminate/drop-weight impact test | Software: LS-DYNA | (1) The simulation results are in good agreement with experimental | Rawat et al. [108] (2020) |
| CFRP plate/analytical model | Using the Mori Tanaka model to analyze the mechanical properties is proposed | When CNTs are distributed in any direction in the composite material layer, the deflection and energy absorption of the plate are larger than when they are distributed in a straight line | Feli et al. [136] (2017) |
| CFRP-CNTs beams/tensile simulations | Using the representative volume element (RVE) model | The impact response of polymeric beams was significantly affected by reinforcing with the combination of CNTs and SCFs | Ahmadi et al. [137] (2018) |
different CNTs concentrations (0.5, 1, 2, and 4 wt%) was studied, and the results confirmed that CNTs had influence on the impact properties of CFRP materials. When the concentration was lower than 2 wt%, CNTs could improve the impact performance of composite materials. However, when the concentration exceeded 2 wt%, the addition of CNTs would reduce the impact performance of the composite material, which might be caused by the deterioration of the internal bonding performance of the composite material due to the agglomeration of CNTs. Tarfaoui et al. [133,134] conducted OHT test on CNT-reinforced CFRP materials according to ASTM D5766 standards [133] and compared with numerical simulations. The Hashin’s criterion and the CZM were used to identify the damage process and the delamination propagation around the hole. Moreover, a layered and linear cohesive zone element (CZE) are used to replace Hashin’s criterion model to accurately predict the damage expansion and the resultant delamination (Figure 22 shows the delamination visualization comparison between the OHT-cohesive model and experimental specimens). The results show that the addition of CNTs can delay the expansion of damage and improve the fracture toughness of the composites. As mentioned earlier, El Moumen et al. [111] conducted Taylor impact tests on CNT-reinforced materials and studied their impact response. They also used the VUMAT to execute in the ABAQUS, realized the establishment and simulation of the numerical model, and compared the simulation data with the experimental results. The simulation results showed that compared with FRP, the CNT-containing FRP had an improved impact energy absorption capacity and significantly reduced the damage of the composite material.

Rawat et al. [108] did the drop-tower impact test on the quasi-isotropic MWCNT-reinforced GFRP laminate, and this was simulated using LS-DYNA. The simulation results were in good agreement with the experimental results, and the visual impact damage morphology under different time steps was obtained, as shown in Figure 23. Feli et al. [136] proposed a new analytical model to study the low-velocity impact response of the CNTs-FRP plates by considering the arrangement and random orientation distribution of CNTs. Through this model, the contact force, deflection history of each layer, the energy absorbed by the plate, and the axial stress and strain were all claimed to be able to determine.

Figure 22: The delamination visualization comparison of OHT-cohesive model and experimental specimens [134].
4 SHM of CNT-FRP

With the rapid and broad application of FRP in many critical engineering structures, nondestructive identification and real-time structural health monitoring of FRP during service are imperative for safety guarantee and cost saving in maintenance [138,139]. The assessment of damage and health monitoring in FRP composites includes traditional NDI techniques [140] such as X-ray [141], ultrasonic testing [142], microwave-related technologies [143], and SHM techniques [144] such as vibration monitoring [145], FBG sensors [138], and acoustic emission [146]. With the increasing application of CNTs [147], their excellent electrical properties are used to improve the electrical conductivity of FRP and identify the damage. CNT networks organize themselves like a nerve-like sensory network within the composite laminate and can potentially act as a tool for SHM of composite structures due to their ability to sense deformation and damage initiation and propagation [139]. This section summarizes the NDI or SHM of CNT–FRP structures with a focus on the role of CNTs in the health monitoring procedure. Table 4 shows some key research on this topic in recent years.

The introduction of CNTs into the composites can improve the conductivity by establishing a conductive network inside the composites. It is expected to reveal the damage state of the reinforced materials during use by detecting the changes in the electrical properties of the CNT conductive network, which requires monitoring of the network resistance in the conductive network of CNT, which is mainly controlled by the contact resistance between the bundles of CNTs rather than by the resistance of CNTs themselves [60,162]. Monti et al. [148] studied the relationship between resistance change and impact damage of GFRP materials after adding MWCNTs and found that there is a relationship between damage and a significant increase in electrical resistance. The experiment preliminarily proved that measuring the resistance of the GFRP material with MWCNTs is a feasible method to monitor the existence of impact damage. Gao et al. [149] monitored the impact damage propagation of CNT-enhanced GFRP materials through in situ resistance measurement by the conductive network formed by CNTs. Experimental results show that its permanent resistance continues to increase during repeated impacts. Meanwhile, the comparative study of multiple methods such as acoustic emission, C-scan, energy absorption, and damage area measurement of FRP composites shows that in situ electrical resistance measurement is a potential way to detect impact damage propagation and monitor the health of FRP structures. Arronche et al. [150] introduced MWCNTs into GFRP to improve its conductivity and used two-point and four-point probe methods to verify and measure its electrical resistance change (as shown in Figure 24). The effect of 50 and 70 J drop-tower impact damage on the electrical
Table 4: Researches on the SHM of multiscale composites of the CNT-reinforced FRP

| Materials         | Test method                                                                 | Reference                   |
|-------------------|-----------------------------------------------------------------------------|-----------------------------|
| CFRP/CNTs         | The real-time sensing behavior of composites embedded with CNT films         | Boztepe et al. [157] (2018) |
| CFRP/bucky paper  | An omnidirectional sensor based on bucky paper sensor is designed to         | Lu et al. [158] (2019)      |
|                   | monitor low-velocity impact damage of composite structures                  |                             |
| CFRP/bucky paper  | CNT films were added to monitor damage propagation at different locations    | Aly et al. [159] (2019)     |
|                   | under impact loads                                                          |                             |
| GFRP/bucky paper  | The EIT method was used to monitor the damage of GFRP materials with CNT    | Shuxuan et al. [160] (2021) |
|                   | films                                                                        |                             |
| GFRP/bucky paper  | The EIT method was used to monitor the damage of GFRP materials with CNT    | Loyola et al. [161] (2013)  |
|                   | films                                                                        |                             |

Figure 24: Schematic diagram of two-point and four-point probe test method [150].

properties of the reinforced hybrid material is experimentally studied, and the results show that the resistance change is not apparent. The research mentioned earlier reveals that adding CNTs in the matrix might help detect impact damage, but the positive effect is not remarkable.

Recently, more research has focused on developing new methods for SHM of composites using CNT films, which can be divided into process monitoring and strain/damage monitoring. CNT films and bucky paper were developed to avoid the problems caused by the dispersion of CNTs at the micro-scale, and their emergence has broadened the scale of carbon nanotubes from micro to macro. Lu et al. [151–154] placed bucky paper made by VFD method in the middle layer of GFRP and investigated the relationship between resin curing and resistance change of bucky paper. Monitoring the storage modulus and damping factor curves during the curing process were used to study the dynamic curing behavior of composite laminates. Finally, the temperature at which the resin reached the lowest viscosity and gel point was determined. Also, it was found that the resistance increased significantly with the increase of temperature through the relationship between temperature and resistance, and finally, it was determined that the point with the highest resistance change rate was close to the point with the lowest resin viscosity.

More research has focused on CNT films for monitoring the change of composite lamination structure under different loading behavior. Wang et al. [155] added BP in GFRP to prepare BP-reinforced GFRP laminates. Through tensile loading tests, the piezoresistive properties of BP and the corresponding tensile strain response of the composites were studied. The results proved that the obtained BP has good piezoresistive performance, and this is affected by the morphology of BP, which will change depending on the applied strain. Huo et al. [156] also prepared BP-reinforced GFRP, performed bending load test, and monitored electrical resistance change. Results confirmed that the position of embedded BP affects the strain response. Also, BP had good self-sensing performance, which could accurately monitor the deformation of the interior and surface of the composite material. Boztepe et al. [157] investigated the real-time sensing behavior.
of composites embedded with CNT films under uniaxial fatigue loads. By cross-laying CNT films in laminated samples (as shown in Figure 25(a)), the mechanic-electrical response of the sensor under the tension–tension fatigue experiment was monitored in the field for 10,000 cycles of loading (as shown in Figure 25(b) and (c)). The experimental results show that the resistance of laminates varies obviously under different damage states, which is possible to monitor the damage accumulation in the fatigue damage process.

Lu et al. [158] designed an omnidirectional sensor embedded in CFRP material by using BP sensors. The BP sensors could measure the change of material resistance in real-time and monitor the low-velocity impact damage of composite structures. The results showed that the sensor could detect invisible damage defects and evaluate the damage propagation in the composite structures. Meanwhile, C-scan of the sensor results was conducted to analyze the experimental results so that the damage location can be determined. Finally, the sensor was still in a stable state after multiple impacts, and it can be used for long-term online monitoring of composite structures. Aly and Bradford [159] inserted two layers of CNT films in GFRP-laminated structures to monitor the damage propagation on the composite structures’ impact side, midplane, and nonimpact side. The results showed that the embedded CNT films could detect, locate, and quantify damage when the main structure was subjected to different types of impacts. Finally, the experiment [159,163–165] conducted that inserting CNT films into laminates could monitor the plane deformation of laminates (Figure 26 shows the samples after impact damage).

Electrical impedance tomography (EIT) is a new measurement technique developed in recent years. Shuxuan et al. [160] have taken advantage of CNT films’ excellent mechatro-electric response to develop self-sensing glass fiber composites for damage monitoring online. The self-sensing composite material measured the boundary voltage by EIT under applying load and presetting damage conditions. Finally, by observing the distribution change of the electrical conductivity in the materials, the location and the size of the damage can be determined. Loyola et al. [161] also used EIT for damage detection. The sensitive characteristics of the MWCNTs distributed in the spatial grid could be used to measure the strain, and the damage detection was achieved by spraying the MWCNTs film on the GFRP material to monitor the spatial distribution of electrical conductivity. The aforementioned studies indicate that the resistance measurements of CNT films may vary in different directions and locations depending on the preparation methods. Meanwhile, CNT films are sensitive to the strain changes of composites. The results showed that resin impregnation could improve the sensitivity of CNT films [166]. However, the high introduction of CNTs in the film will also reduce the resistance sensitivity.
The emergence of CNT films and bucky paper in various SHM fields has increasingly highlighted its engineering application value. However, to achieve engineering applications, they must further improve the sensitivity, accuracy, and response speed of monitoring for different monitoring circumstances. Meanwhile, a more completed accuracy evaluation standard should be established by referring to the traditional high-precision offline monitoring method. As the production cost of CNT-enhanced FRP reinforcement materials is reduced, these composites can be more widely used in different fields such as SHM and in situ NDI in the future.

5 Summary and perspective

The purpose of this article is to review the research work on CNT-reinforced FRP composites. The various preparation methods of CNT-reinforced FRP materials, the effect of adding CNTs nanofillers on the interlayer crack resistance, impact, and fatigue resistance properties of FRP were all covered in the paper. Besides, this review article also has summarized the up-to-date research on NDI and SHM of CNT-FRP materials.

In more than two decades, the preparation, processing, and microstructure control of CNT-enhanced multiscale hybrid FRP materials have become increasingly mature. With the applications of two-dimensional CNT films and bucky paper, CNT-enhanced multiscale hybrid FRP materials have also made significant progress in terms of macrostructures. The current research on the enhancement mechanism of CNT-enhanced multiscale hybrid FRP materials has become clear: the addition of CNTs/CNT films enables FRP to resist the initiation and expansion of cracks and the enhancement effect under the macroscopic form. CNTs can greatly improve the
weak mechanical properties of the matrix of traditional FRP materials and enhance their resistance to delamination damage caused by impact. At the microscale, microscopic images of the experimental materials were observed and analyzed through various observation methods such as SEM and TEM, so that to understand the mechanism of enhancement by CNTs embedded in FRP, that is the CNTs are working as bridges and only allowing the whole pull-out. However, the current research has still left some gaps to be filled: (1) The numerical simulation of CNTs- FRP materials needs to be developed. For instance, with macroscopic simulation, there is no reliable failure criterion to simulate the failure of CNT-FRP structures in the finite element model. (2) The NDI and SHM of the CNT-FRP structures are not yet studied comprehensively, but this is an inevitable problem since the CNT-FRP are expected to be used mostly as key components in applications. (3) Currently, the application of CNT-enhanced multiscale hybrid composite materials still has a long way to go from laboratory-scale studies to actual industrial-scale production and life. CNTs are dispersed in different polymers with uneven dispersion, agglomeration at high concentrations, and lack of good alignment and arrangement in the matrix. Newer manufacturing processes, such as the CNT film and bumpy paper, provide a potential solution, but more work is needed to establish the large-scale application of these materials. Cost is also a major limiting factor in the industrial adoption of CNT-enhanced FRP composites. Although some companies have successfully applied these materials to industries such as aerospace, marine transportation, and sporting goods, the high production costs limit the use to some special customized situations. At the same time, there is not enough research conducted on the actual application of the material in the existing literature research, and most of the researches are still exploring more excellent preparation methods and better material properties. In the future, if CNTs are to be applied to reinforced FRP materials on a large scale, it is necessary to have excellent production technology with high performance, low cost, and impurity-free CNT on the premise of mass production.

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