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# Building Hierarchical Micro-Structure on the Carbon Fabrics to Improve Their Reinforcing Effect in the CFRP Composites

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Additional information is available at the end of the chapter

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## Abstract

Nano-fibers grafted on carbon fibers (CFs) has been of one of the most popular methods used for the carbon fibers surface treatment, which could significantly influence the interfacial properties between polymer matrix and carbon fibers in composites. This chapter demonstrated three novel carbon fibers surface treatment methods, they are carbon nanotubes (CNTs) grafted on CFs using catalysts formed in an ethanol flame, carbon fiber forests (CFFs) by carbon fiber surface brushing and abrading and ZnO nanowire grown onto CFs through a facile hydrothermal method respectively. Based on metal catalyst particles or dopamine-based functionalization formed onto the nano-fiber/CF interface, a good interfacial bonding strength between the nano-fiber and CFs was observed by an instrumented tip of an atomic force microscope and further improvement of interfacial shear strength with epoxy as measured by the single fiber pull out/microbond test was realized. The hierarchical micro-fibers on CF fabrics were then utilized to fabricate the laminates to characterize anti-delamination capacity (the mode I and mode II interlaminar fracture toughness) of these composite laminates, wherein carbon fiber fabrics were grafted with CNTs, short CFs and ZnO nanowires respectively.

**Keywords:** CNTs forests, ZnO nanowires, interfacial bonding, anti-delamination

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## 1. Introduction

Carbon fiber reinforced polymer (CFRP) composite laminates have been widely used in weight-critical structures, such as aircraft, spacecraft, and racing cars, due to their excellent mass-specific mechanical properties. However, poor interlaminar toughness has become an

important limiting factor in practical structural applications. To overcome the deficiencies in through-thickness strength, lots of techniques were developed to improve the interlaminar fracture toughness of CFRP composites by toughening the resin with various reinforcements [1]. Although toughened bulk resins exhibit higher toughness value, they only provide limited improvement on the delamination resistance in the CFRP composites in most cases due to the limitation by the carbon fibers [2]. Moreover, some processing problems were inevitably caused by the increasing viscosity of the resin due to the presence of high content of fillers. The challenge remains, therefore, to develop a new solution to facilitate practical applications of such composites as reliable and robust structural material.

The building up of hierarchical multi-scale reinforcement for CFRP composites by directly attaching or in situ growing micro-structure onto the fiber surface has been demonstrated as an efficient method for improving reinforcing properties of the composites. Moreover, grafting micro-structure onto carbon fibers (CFs) has been shown to improve the interfacial load transfer in polymer composites by fiber pull-out and fiber fragmentation tests [3]. Two major interfacial interactions, that is, micro-fiber/polymer and micro-fiber/CF, are believed to contribute to the improved mechanical properties. The advantages of this technique over the ones of attaching the preformed micro-structure mentioned above could be better dispersion, higher density, and even orientation control in the composites.

This chapter proposes a comprehensive and systematic view of improving the reinforcing effect in the CFRP composites by three typical hierarchical micro-structures including CNTs on CFs, CFFs on CFs and ZnO NWs on CFs. Firstly, we will demonstrate that the simple method allows the CNTs to be readily grafted onto CF mats for interfacial strength and fracture toughness enhancement. The objective of this work was to grow CNT effectively on carbon fabrics by a simple flame synthesis method and to characterize their effects on the interfacial properties and fracture toughness of the CFRPs. Next, we review our recent work on the toughness improvement of carbon fiber/epoxy composites by brushing and abrading of the woven fabrics. At last, we propose a novel dopamine-based functionalization method to improve the interfacial adhesion between ZnO NWs and CFs. Carbon fiber was modified with dopamine, and then ZnO nanowires were grown onto the modified carbon fibers by a facile hydrothermal method. The chapter concludes with a summary and comparison of existing toughening methods.

## **2. Hierarchical carbon nanotubes forests on carbon fibers**

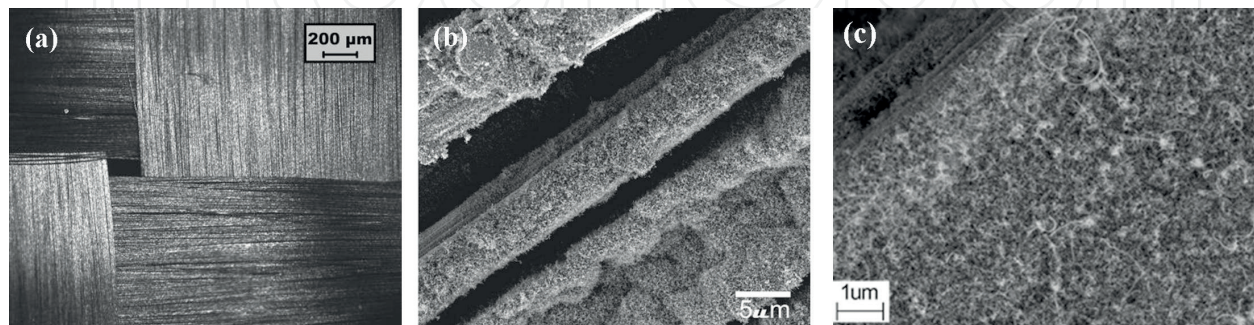
Carbon fiber is a multifunctional reinforcement for FRPs due to its light weight, good chemical and thermal stability, high electrical and thermal conductivity, and mechanical properties as well. It is suitable to be used as fiber substrate for in situ growing CNTs as its high thermal stability can withstand the temperatures for the process. Therefore, the building up of the hierarchical carbon reinforcement can be also achieved by in situ growing CNTs onto CFs and it was demonstrated to be an efficient way to interfacial improvement of carbon fiber reinforced composites (CFRPs) [4]. CNTs could be directly applied onto the fiber surface by

the spreading of CNT powder [5] or CNT-solvent paste [6], and transferring CNT arrays [7]. Grafting of CNTs onto CFs could also be achieved by the chemical reaction between the pre-modified functional groups on the surface of both CNTs and CFs [8]. The electrophoresis technique could also been employed [9], where CNTs were uniformly deposited on the surface of carbon fabric from the CNT dispersion in an electric field. Among the various in situ growing CNTs methods, chemical vapor deposition (CVD) could be the most utilized method for growing CNTs onto CFs [10], even though it is an energy intensive batch process and requires costly reagents and equipment. Great interfacial improvement and good adhesion between CNTs deposit by CVD and CFs has been demonstrated [11].

Comparing with CVD methods, the flame growth of CNTs onto CFs is developed very recently and the strong adhesion of in situ flame synthesized CNTs onto CF was demonstrated by direct measurement of the force for peeling single CNT from CF [12]. These imply possible interfacial improvement of the CFRPs by the flame growth of CNTs onto CFs. On the other hand, the oxygen-functional groups have been proved to be formed on the surface of the flame synthesized CNTs [13], and their existence was believed to be an advantage of the flame synthesized CNTs over the conventional CNTs by CVD. In addition, for the method of in situ growing CNTs onto CFs, a great challenge is to prevent the mechanical degradation of the CFs by the intense heating using normal CVD techniques (usually above 700°C and tens of mins or even more), as evident mechanical degradation of the fiber has been observed [14]. In the view of commercial application, it is highly desirable that the mechanical properties of CFs in the hierarchical carbon structure are retained.

## 2.1. The preparation and characterization of flame synthesized CNTs onto CF

The growth of CNTs was performed by Du et al. [12, 13] though inserting the CF mats with  $\text{NiCl}_2$  catalyst into the core of the flame, where the temperature is about 500–700°C. Both tip growth mechanism and root growth mechanism are found to be involved in the flame growth process. The CNT growth time is several minutes and the process is adopted in an open environment. Compared to the optical image of bare carbon fabric (**Figure 1a**), entangled CNTs uniformly grown on the surface of the CFs and SCF can be observed in SEM image (**Figure 1b**). By analysis of the CNTs scratched from CF mats and dispersed them in ethanol,



**Figure 1.** (a) Optical image of carbon fabric [13]; (b) SEM image of CNT/CF growth for 3 min [13]; (c) SEM image of CNT/SCF growth for 3 min [18].

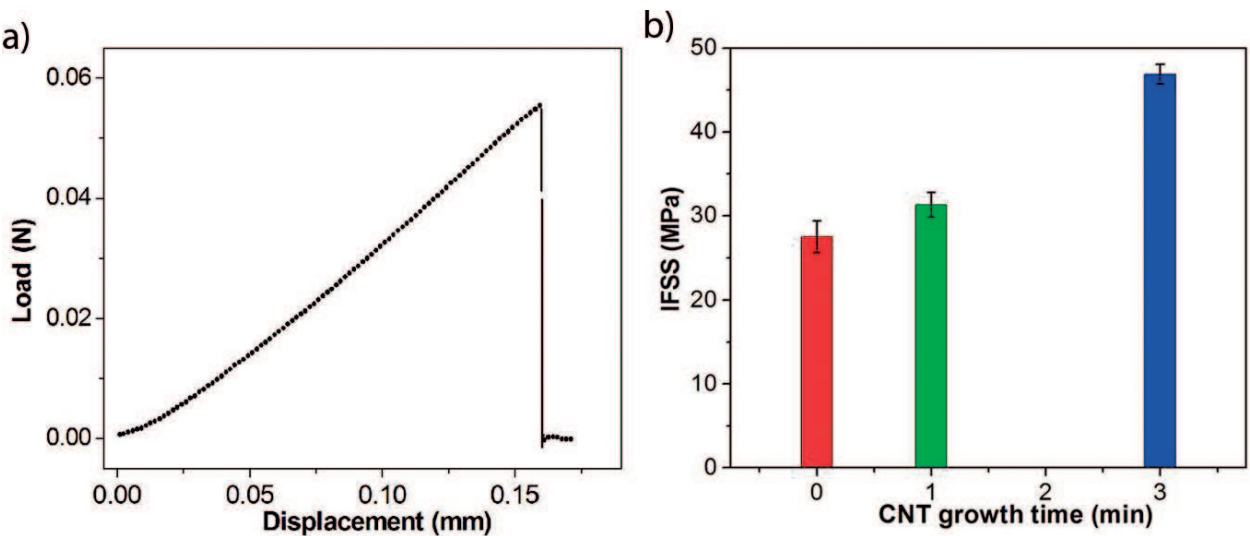
the length of most CNTs growth 3 min are observed to be roughly 1–2  $\mu\text{m}$ , much larger than the ones growth for 1 min (always <500 nm). Another synthesized CNTs onto CF system is based on short carbon fibers (SCFs), which were prepared by cutting plain woven carbon fiber fabrics. The diameter and average length of SCFs were about 7  $\mu\text{m}$  and 750 ( $\pm 200$ )  $\mu\text{m}$ , respectively. Then, CNTs grew on the SCF surface by the ethanol flame synthesis method for 3 min, and their morphology is displayed in **Figure 1(c)**.

Moreover, the single fiber tensile testing results indicates the growth of CNTs on the surface of the fiber does not result into any evident decrease in fiber tensile strength, demonstrating the advantage of our flame growth method over those previous reports with other techniques, where the tensile performance decreased more or less [14].

### 2.2. Interfacial shear strength

The concept of in situ growing CNTs on the surface of CFs has been introduced to increase the interfacial shear strength of CFs in the matrices [4]. The growth of the CNTs on the surface of CFs leads to the formation of two interfaces: one between the CF and CNT and a second between the CNT and polymer matrix. Outstanding adhesion between CNTs deposit by CVD and CFs has been demonstrated [4]. According to the single fiber fragmentation test, there was a dramatically increase in the interfacial shear strength after the CNTs grafted onto CFs [15]. The bonding of CNTs to CF was so strong that the failure occurred within the CF surface rather than the interface and the outlayers of CFs were even peeled off during the fracture process [16]. In a recent work, the strong adhesion of in situ flame synthesized CNTs to CF substrate was demonstrated by measurement of the force for peeling single CNT from CF [12]. This demonstrates a good possibility for increased interfacial shear strength and fracture toughness of the CFRPs by the flame growth of CNTs onto carbon fabric reinforcement.

Typical pull-out load versus displacement of the single fiber pull-out test for CF grafted with CNTs for 3 min was shown as **Figure 2a** conducted by Du et al. [17], where the load increases



**Figure 2.** (a) The pull-out load versus the displacement [17]; (b) the interfacial shear strength versus CF with CNT growth in different time [17].

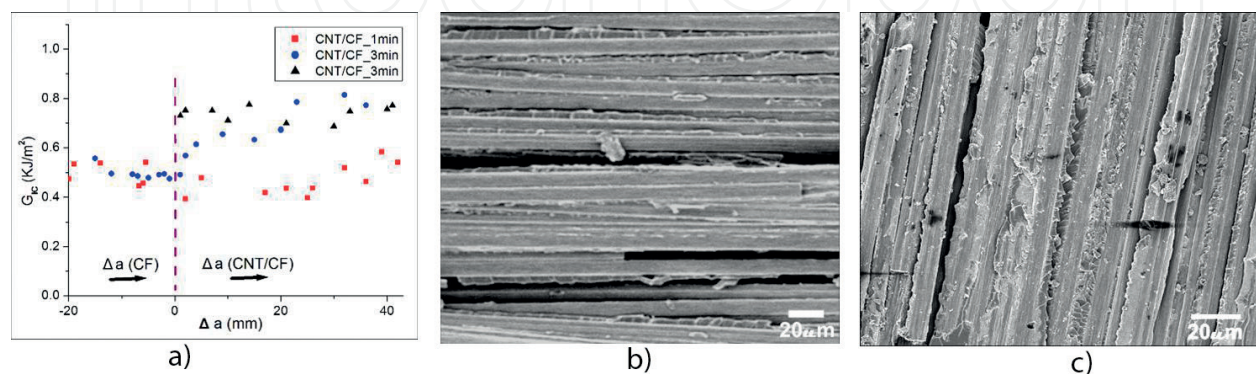


almost linearly with the displacement until the peak load is reached, followed by a sudden drop to zero, indicating the instantaneous debonding of the fiber-matrix interface. As shown in **Figure 2b**, the modification with CNTs significantly increases the IFSS by 70.5% with the interface of CNT growing for 3 min, however, the modification with CNTs growing for 1 min has no significant effect on the enhancement of the interfacial properties. The results here demonstrate that the interfacial properties can be significantly promoted and controlled by tuning the factors of flame growth CNTs. It is expected that the enhanced IFSS measured with the single fiber pull-out test could transform into the improved the fracture toughness properties of the lamina.

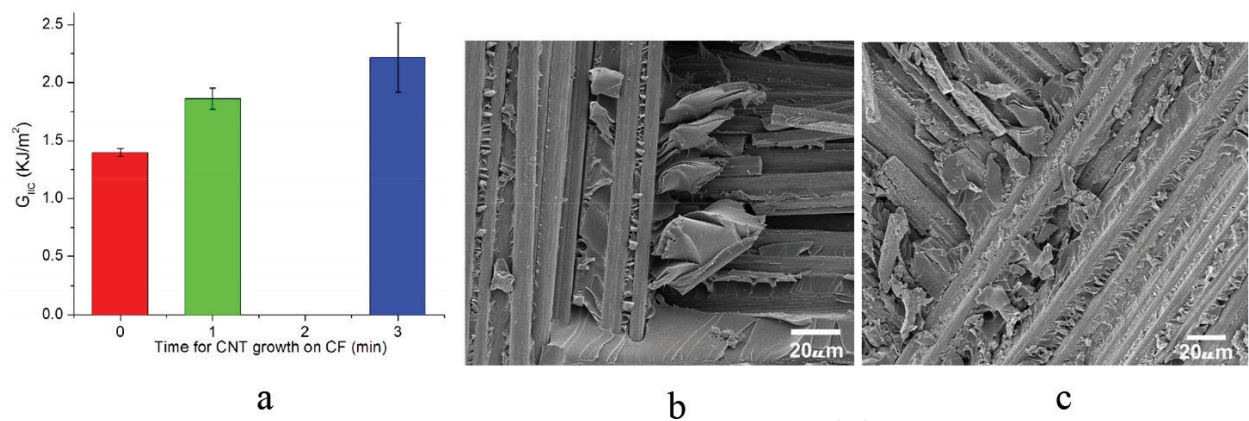
### 2.3. Interlaminar fracture toughness

Typical energy release rate as a function of the crack growth (*R*-curves) for CF grafted with CNTs growing for 3 min is shown in **Figure 3a**, conducted by Du et al. [13]. It can be clearly seen that the modification with CNTs lead to significantly increased fracture toughness. For the lamina with CNTs growing for 3 min onto carbon fabrics, the average  $G_{IC}$  increases by 67% comparing with those with bare carbon fabrics. Similar research on the effect of the grafting of CNTs onto CFs on the mode I fracture toughness of laminates shows a ~46% increase of  $G_{IC}$  after the CNTs growing onto carbon plain woven by CVD [10]. From the SEM image (**Figure 3b, c**) [13] of the mode I fracture surface of laminate reinforced with bare CF and CNT/CF, it can be found that there exists improved interfacial adhesion between the fiber and matrix after the flame growth of CNTs onto carbon fabrics. The increased interfacial adhesion results into the cohesive failure of the matrix. This indicates that the CNTs have strong bonding with the CFs.

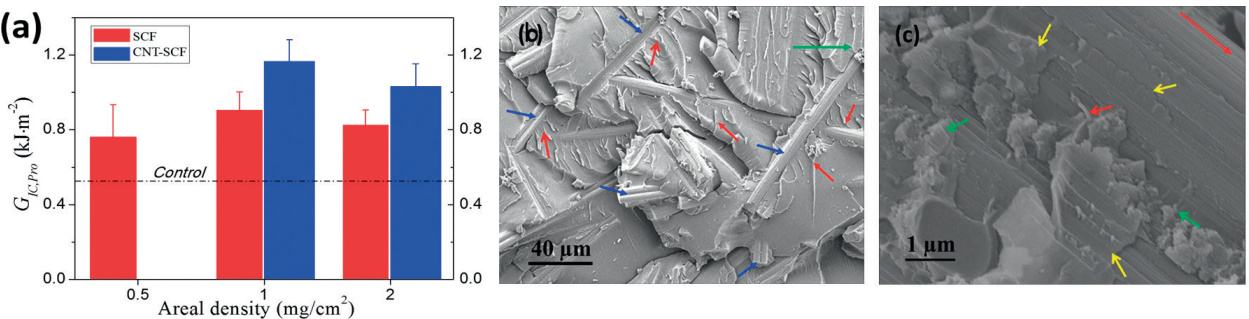
Similarly, as shown in **Figure 4a**, the modification of the carbon fabrics by in situ flame growth of CNTs also shows great effect on the mode II fracture toughness of the lamina. The average  $G_{IIC}$  of the lamina, increases from 1.40 kJ/m<sup>2</sup> for the bare carbon fabrics to 2.22 kJ/m<sup>2</sup> for the ones modified with CNTs growing for 3 min, or a ~60% increase [13]. After the modification with CNTs, the zipper-like patterns can still be observed in the area with CF bundles parallel to the crack propagation, as shown in **Figure 4b**. It can be observed that the grafting of CNTs increase the number of zipper-like patterns (**Figure 4c**), which corresponds to a clear increase in  $G_{IIC}$  in the laminate with the insert crack.



**Figure 3.** (a) Typical *R*-curve for mode I interlaminar fracture of the laminate; (b) SEM image of the mode I fracture surface of laminate reinforced with CF baseline and (c) the CNT/CF [13].



**Figure 4.** (a) The mode II interlaminar fracture toughness of the laminate,  $G_{IIc}$  versus CNT growth time; (b) SEM image of the mode II fracture surface of laminate reinforced with CF baseline and (c) the CNT/CF [13].



**Figure 5.** (a) The mode I interlaminar fracture toughness of the laminate; (b) SEM image of the mode I fracture surface of laminate reinforced with SCF and (c) the CNT-CF-SCF [18].

The influences of SCF and CNT-SCF interleaves on mode I interlaminar fracture initiation  $G_{IC}$  of CFRP laminates are also discussed in our previous work [18]. As **Figure 5a** shown, the materials tested were: (a) CFRP without any interleave (control), CFRP with (b) SCF or (c) CNT-SCF interleaves of areal density 0.5, 1.0 and 2.0  $\text{mg/cm}^2$ . The experimental results showed that, compared to the control, SCF interleaves with areal density of 1.0  $\text{mg/cm}^2$  did not have much effect on  $G_{IC, Ini}$  (0.48 vs. 0.51  $\text{kJ/m}^2$ ); however, the CNT-SCF interleaves with areal density of 1.0 and 2.0  $\text{mg/cm}^2$  increased  $G_{IC, Ini}$  of the control by 0.14 and 0.31  $\text{kJ/m}^2$  to 0.62 and 0.79  $\text{kJ/m}^2$ , respectively, hence confirming the higher toughening effect afforded by the CNTs adhered onto the epoxy matrix. Compared with characteristic brittle fracture of epoxy between adjacent CFs in the control CFRP laminates as shown in **Figure 3b**, **Figure 5b** shows clearly rugged and multi-planar fractures typified by brittle failure of epoxy with intense river marks around both debonded and dislodged SCFs lying more or less flat on the fracture surface. Moreover, as **Figure 5c** shown, clusters of CNTs may break or pull-out when the lowly embedded SCFs are debonded from the matrix leaving behind residual holes on the track. This action provides extra toughening of CNT-SCF interleaves due to CNT bridging and pull-out that are absent in SCF-interleaves.

Comparisons of  $G_{IC}$  of typical CNT-modified CFRPs in the literatures are given in **Table 1**. As the table shown, it can be seen that the enhancement of  $G_{IC}$  value of laminated composites modified by flame synthesis method in Du's work [13] is a little larger than the laminated

CNT grafted region	Test method	Toughness improvement	Ref
Growing CNT by CVD	DCB	46% (Mode-I)	[10]
Growing CNT by flame synthesis method	DCB	67% (Mode-I)	[13]
CNT grafted short carbon fibers	DCB	125%(Mode-I)	[18]

**Table 1.** Improvements in the fracture toughness of typical CNT-modified CFRPs.

composites modified by CVD method [10], which is possibly due to the better adhesion of in situ flame synthesized CNTs onto CF [12]. Moreover, flame synthesized CNTs grafted short carbon fibers interleaved laminated composites shows the remarkable toughness improvement among the CNT-modified CFRPs, this is because the hierarchical short carbon fibers interleave contribute the toughness improvement additionally.

### 3. Hierarchical short carbon fiber forests on carbon fibers

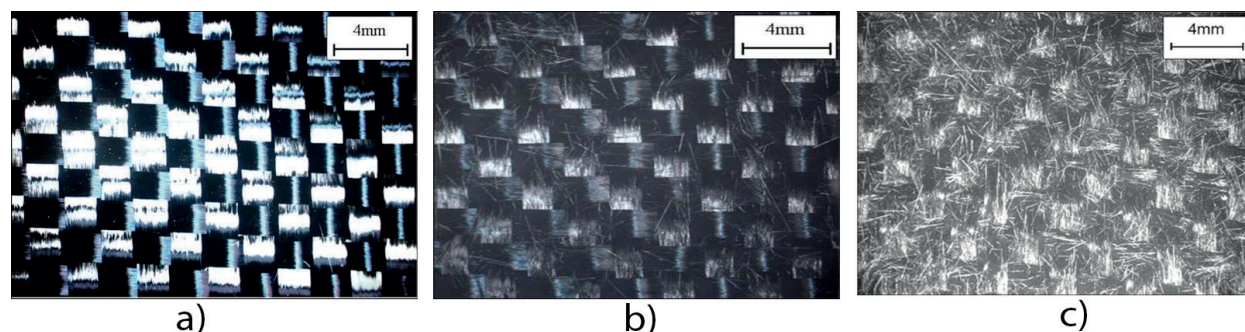
Up to now, there is limited report on the enhancement of the interfacial properties between fabric and matrix in laminates by increasing the surface roughness of fabric directly. In this section, fuzzy fabrics were prepared with a simple fabric surface brushing and abrading method. With this method, the carbon fiber forests (CFFs) will be fabricated in situ on the surface of the continuous woven carbon fabrics. In the CFRP composite reinforced with the modified fabrics, the CFF is expected to be distributed uniformly in the epoxy rich area in the interlayer of the laminates and acts as interleaf. Moreover, different from the previous interleaving method with additional materials being put into the interlayer, one of the advantages of our in situ produced CFF interleaves is that they adhered well to the fabrics as some fibers of them root in the carbon fabrics, which is believed to provide better delamination resistance. And its 'green' manufacturing process is much more cost-effective, chemical-free, and environmental friendly.

#### 3.1. The morphology and characterization of short carbon fiber forests

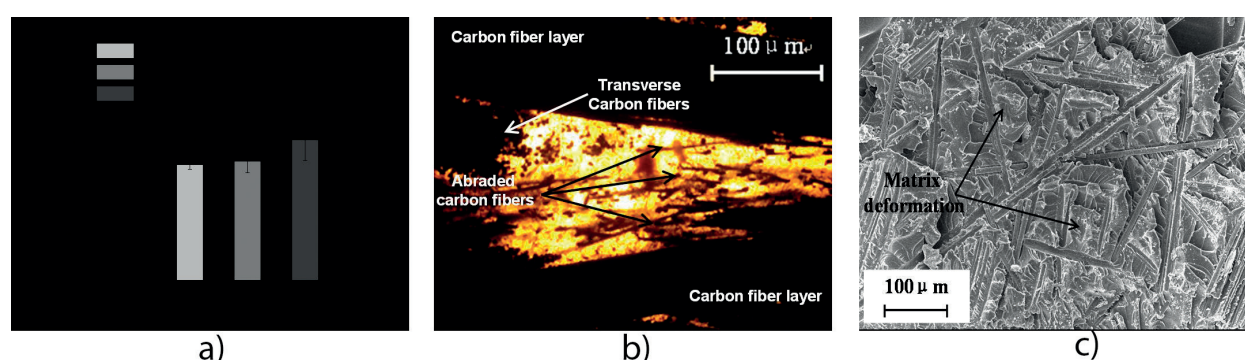
The carbon fiber forests were fabricated through a brushing and abrading process on one side face of woven carbon fiber cloth. **Figure 6** exhibited the evolution of the morphology of fiber fabrics after different brushing and abrading times, respectively.

As shown in **Figure 6a**, the carbon fiber bundles in the original plain woven carbon fabrics are continuous and interweaving across each other, and the fabric surface texture is clean and tidy. As the abrading times increase, the broken carbon fibers are increased, and correspondingly, the fabric surface texture become more defective and rougher(**Figure 6b–c**). Moreover, it can be seen that broken carbon fibers are uniformly and randomly distributed on the surface of the fabrics and form a fiber forest. No fiber bundles/aggregation separated from the fabrics was observed. These indicate that the original fiber bundles were partially damaged and some broken carbon fibers in the bundles tend to stand up from the in-plane of the carbon fabrics.





**Figure 6.** The surface morphology of (a) original carbon fabric; (b) carbon fabric abraded by 5 times; and (c) carbon fabric abraded by 30 times [32].



**Figure 7.** (a) Toughness of CCFs toughened laminate; (b) the optical images of the mid-layer of laminates interleaved by CFF; (c) the mode I fracture surface morphology of CFF interleaved CFRP composites [32].

### 3.2. Interlaminar fracture toughness of CFRP composite laminates with hierarchical short carbon fiber

As shown in **Figure 7a**, the delamination resistance of the modified laminates depends on the brushing times. The fracture toughness of the composites increased slightly and slowly over that of the baseline composite with the increasing abrading times from 5 to 20. When the abrading time was further increased to 30 times, the significant increase of the mode I fracture toughness of CFRP composite occurred, where GIC is increased by 62.4% for composites interleaved with one layer of CFF. Further improvements of the delamination resistance up to 83.2% can be achieved by the modification of both plies with CFF on their surface. These provide versatile designs of the laminate structure with the enhanced interlaminar fracture toughness in certain inter-layers. The significant improvement of the delamination resistance by 30 abrading times implies that the establishment of the effective 3D fiber network in the interlayer, which resists the crack opening efficiently. **Figure 7b** shows the morphology of CFF in the interlayer of CFRP composite. It is observed that carbon fibers in the interlayer of composite were random distributed, and the tips of some carbon fibers were separated from surrounding fiber bundles and randomly exposed out of the matrix region in the interlayer. Such a CFF structure was expected to interlock/ intersect each other in the narrow matrix region in the interlayer and formed a interwoven network structure, which potentially help to retard the crack propagation efficiently. To better understand the mechanism of the CFF

Reinforcement material for laminate	Test method	Fracture toughness increment (%)	Ref
SCF tissue	DCB	~5 to 28	[21]
CNT-SCF tissue	DCB	98–125	[18]
CNT forests by flame	DCB	67	[13]
CNT forests by CVD	DCB	31–61	[10]
CFF by brushing method	DCB	62.4	[32]

**Table 2.** Improvement on the interlaminar fracture toughness of CFRPs with various reinforcements.

interleaved CFRP composites, the fracture surfaces of samples after DCB test was studied by SEM (**Figure 7c**), where one could see that carbon fibers in the CFF were separated from the original carbon fiber bundles and randomly distributed in the fracture surface. The toughness enhancement of the fiber reinforced composites could be attributed to observed several generally accepted mechanisms, including fiber breakage, fiber-matrix debonding, fiber pull-out and matrix plastic deformation.

**Table 2** gives some literature results on the mode I interlaminar fracture toughness for CFRP composites modified by various hierarchical short fibers such as SCFs [18], Kevlar fibers [19] and CNTs [13]. It can be seen that the enhancement of  $G_{IC}$  value of CFRP composites modified by brushing method is obviously among the best results, and there is no additional interleaving materials for the CFRP composite as the CFF is created in situ by the surface brushing and abrading of the fabrics themselves. Although both the CFF and SCF tissue are composed of carbon fibers, they display different morphology in CFRP composite. The carbon tissues were composed of chopped short carbon fibers with ~15 mm in length [20], which were mainly aligned in the in-plane direction of the laminates. In contrast, CFFs in the interlayer are expected to be distributed randomly in 3D directions, which demonstrates efficient crack bridging for toughness improvement. Furthermore, the morphology of well-adhesion of CFF interleaves to the fabrics in the CFRP composite revealed in **Figure 7b** is superior to the SCF tissue interleaves [18], in which SCF was additionally inserted into the interlayer of carbon fabrics without any bonding force to adjacent fabric plies.

#### 4. Multifunctional ZnO nanowires grown on carbon fibers

Because of their unique magnetic, piezoelectric and optical properties, ZnO nanowires have been widely used in energy and environment applications [21–25]. Carbon fiber, which has been extensively used in light-weight structures, is a good support for ZnO because of its excellent electrical properties and flexibility to hybrid material, therefore, the established ZnO nanowire-carbon fiber hybrid materials can be used in highly wearable and stretchable supercapacitors, flexible piezoelectric generators and quantum dot-sensitized solar cells. The preparation, multi-functionality and application of ZnO nanowire-carbon fiber hybrid materials were mainly investigated in most previous studies, and few efforts were made to characterize the mechanical properties of this hybrid material. Actually, the mechanical properties, particularly,

the interfacial adhesion strength between the carbon fiber and ZnO NWs, play a key role in their application. For example, the ZnO NWs may easily fall off the carbon fiber in service if the interfacial adhesion between carbon fibers and ZnO NWs is relatively weak, which may lead to degradation of the material performance and possible material failure in further. So it is critical to investigate the interaction between ZnO NWs and carbon fibers and further clarify the adhesion mechanism.

CF/ZnO NWs has intrinsically poor interfacial adhesion because of insufficient functional groups on the CF surface that connects with ZnO, the current chemical oxidative methods including acid or plasma treatments are utilized to introduce the functional groups onto the CF surface to improve the CF/ZnO NWs interfacial adhesion, but oxidation functionalization can etch the fiber substrate and thus decrease the CF strength, which is undesirable for all applications. To address this problem, we [26] recently introduces Polydopamine (PDA) onto the CF surface to bond with the ZnO NWs, because PDA owns a robust chelating capability toward metal ions and can act as nucleation sites to form a metal oxide-PDA core/shell structure, the experimental results showed uniform and vertical aligned ZnO nanowires are well grown in the CF surface modified by PDA. In fact, the formed PDA layer has many functional groups such as quinone, carboxyl, catechol, amino and imino groups, which formed the main interaction, namely, the coordination between the catechol groups and the  $\text{Zn}^{2+}$  ion, this interaction gradually promotes the ZnO seed layer, from which ZnO NWs are nucleated and grow on the PDA-modified CF.

4.1. Pull-out force and strength of ZnO NW from CF

The adhesion strength between ZnO NWs and CF modified by PDF is the key factor to evaluate the PDA bonding effect between ZnO NWs and CF. Thus, it is necessary to measure the adhesion force between ZnO NWs and CF. Similar work has been done by Sodano et al., who have investigated the interaction between ZnO and graphite [27]. They applied a ZnO nanoparticle coated AFM tip close to the surface of highly oriented pyrolytic graphite to study the interaction between ZnO and carbon substrate. Although their method can, to some degree, reflect the interaction between ZnO and graphite substrate, real adhesion force between ZnO and carbon fibers cannot be measured. So it is necessary to develop a concise and direct method to measure the adhesion force and adhesion strength between CF and ZnO NWs. Recently, we [26] measured the pull-off force of ZnO NW from CF though a nano-manipulator equipped with a sensitive force measurement system inside the SEM chamber. **Table 3** gives the pull-out force and adhesion strength between bare or PDA-modified CFs

Hierarchical CFs	ZnO NW diameter (nm)	Pull-out force (N)	Adhesion strength (MPa)
CF/ZnO	300	1.65 ± 0.3	23.32 ± 4.56
CF/ZnO	700	8.7 ± 0.55	22.61 ± 3.68
CF/PDA/ZnO	300	4.2 ± 0.89	59.41 ± 5.32
CF/PDA/ZnO	700	27.5 ± 1.75	71.45 ± 8.54

**Table 3.** Pull-off (adhesion) force and adhesion strength between ZnO NW and CFs.



and ZnO NWs with different diameters of ZnO NW [26]. It can be seen that the pull-off force between PDA-modified CF and ZnO NW is much larger than that between bare CF and ZnO NW for a given ZnO NW diameter, which indicates great pull-out force improvement between CF and ZnO NW when PDA is introduced. Similar increase for the adhesion strength is also observed.

#### 4.2. Interfacial strength of ZnO NW grafted CFRP composite

The interfacial shear strength (IFSS) of carbon fiber/epoxy composites was characterized by Zheng et al. [26] using the single fiber microbond tests. The results show average IFSS of bare CFRP is improved by 47% after ZnO growth owing to the mechanical interlock led by the penetration of stiff ZnO NWs into the epoxy resulting in an increased bonding area. Some results indicate that failure during the microbond experiments generally occurred at the ZnO NWs/fiber interface [28, 29]. However, there is no ZnO NWs found on the debonded surface of the pulled out CF, implying that all ZnO NWs were sheared off from the CF and embedded in the epoxy, so it can be concluded that failure occurred at the CF/ZnO interface, which limited further increase of the IFSS more or less.

#### 4.3. Interlaminar fracture toughness of CFRP composite with hierarchical CF/ZnO fibers

Since ZnO NWs on CF are similar to toughening methods such as z-pinning [30] and CNTs grown on CFs [13], CF/ZnO hybrid composites can be used to manufacture laminates for the aerospace applications. Z-pinning and CNTs grown on CFs techniques have been applied in laminates for interlaminar toughening but some loss of in-plane strength may occurred in them, which is undesirable for laminate applications. By contrast, the hierarchical CF/ZnO NWs is prepared under low temperature without strong acid treatment, thus retaining the CF strength [31]. In addition, unlike CNTs which may collapse easily on the CFs during epoxy infusion, the rigid ZnO NWs can maintain their upright geometry during processing and provide strong mechanical interlocks with epoxy matrix [31] thus yielding more effective toughness improvement for composite laminates, hence, we [26] conducted the Double-cantilever-beams (DCB) and three-point end notched flexure (ENF) tests to evaluate mode I and mode II interlaminar fracture toughness of CF/ZnO NWs laminates. As **Figure 8a** shown, the fracture toughness of control laminate is  $0.49 \text{ kJ/m}^2$  and this value is increased by 43 and 63% with introducing CF/ZnO NWs and CF/PDA/ZnO NWs, respectively. Mode II fracture toughness value for three types of laminates can be found in **Figure 8b**, which are 1.4, 1.61 and  $1.71 \text{ kJ/m}^2$  for the Control, CF/ZnO NWs and CF/PDA/ZnO NWs modified composites laminate, respectively, indicating 15% and 22% increases respect to the Control. It can be concluded that both mode I and mode II interlaminar toughness of CF/ZnO NWs laminates were indeed found to be increased, and further increases in these toughness values were achieved for the CF/PDA/ZnO NWs hybrid laminates due to the enhanced interfacial interaction between ZnO NWs and PDA-modified CF.

**Table 4** gives existing results on the mode I and mode II interlaminar fracture toughness for CFRP composites modified by various hierarchical reinforcement such as ZnO NWs [26], SCF



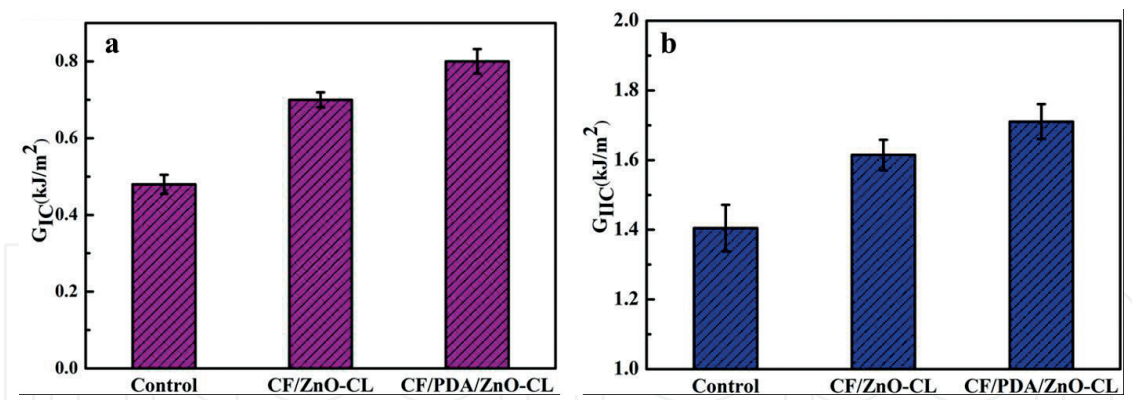


Figure 8. (a)  $G_{IC}$  and (b)  $G_{IIC}$  of three types of CFRP composite laminates [26].

Reinforcement material for laminate	Test method	Fracture toughness increment (%)	Ref
ZnO NWs	DCB	43–63	[28]
	ENF	15–22	
SCF tissue	DCB	73	[18]
CNT-SCF tissue	DCB	125	[18]
CNT forests by flame	DCB	67	[13]
	ENF	59	
CFF by our brushing method	DCB	62.4	[32]
	ENF	83.2	

Table 4. Improvement on the interlaminar fracture toughness of CFRPs with existing hierarchical reinforcements approaches.

tissue [18], CNT-SCF tissue [18], CNT forests by flame [13] and CFF by brushing method [32]. It is noticed that the interlaminar fracture toughness of composites laminate with ZnO NWs is lower than composites laminate with carbon reinforcement. It can be seen that the hierarchical short carbon reinforcement (see SCF tissue or CFFs in Table 4) or flame synthesis CNT forests could only give the limited toughness improvement for laminate while CNT-SCF tissue exhibits the highest toughness improvement due to its synergistic effect with incorporation of CNTs and SCF.

The toughening mechanisms in mode I and mode II was conducted [26] as well, it is found that the interlaminar failure largely occurs at the CF/ZnO NWs interface which consists with the single fiber microbond pull-out tests. It is claimed that the increased toughness mainly comes from the large matrix deformation induced by the ZnO NWs. From the CF/PDA/ZnO NWs, the cohesive rather than adhesive failure during crack propagation could be the main toughening mechanisms, ZnO NWs strongly bonded on CF can serve as pin-like materials. Their toughening effect works by a crack-wake bridging mechanism that includes their spanning across the matrix crack, thereby, increase the mode I and mode II interlaminar fracture toughness.

## 5. Conclusion

In this chapter, three novel carbon fibers surface treatment methods, typically carbon nanotubes (CNTs) grafted on CFs using catalysts formed in an ethanol flame, carbon fiber forests on carbon fibers, ZnO nanowire grown onto CFs through a facile hydrothermal method respectively, were presented and detailed. The conclusions are as follows:

Firstly, the flame synthesis method is demonstrated to be an efficient technique for the in situ growth of CNTs onto the surface of carbon fabric to build up the hierarchical reinforcement in multi-scale laminate composites for improved interfacial and fracture properties. The CNTs growing temperature is as low as 450°C and the tensile performance of single carbon fiber did not degrade evidently after the CNTs deposition. The flame synthesized CNT interface developed here has been shown to offer a significant enhancement in the interfacial properties. ~70% increase of IFSS was achieved after the modification by flame growth CNTs for 3 min onto CFs. The  $G_{IC}$  and  $G_{IIC}$  of the composite reinforced by carbon fabric with CNTs growth for only 3 min could be enhanced about 60 and 67% over those without CNT grafting, respectively. Analysis of the surface following failure showed the lamina samples reinforced with bare carbon fabric were dominated by adhesive failure while the CNT-modified ones were predominantly cohesive matrix failure. The simple and open environmental deposit process together with the decreased growth time of the flame synthesis method make it a promising technology to fabricate hierarchical carbon reinforcement.

Secondly, the presented simple surface brushing and abrading method was demonstrated to significantly enhance the delamination resistance of the composite with moderate in-plane tensile strength loss. The fabric surface brushing and abrading method was simple, economic, environment friendly and chemical free. Moreover, there is no any additional reinforcement applied in the composites. Furthermore, the defective fabric surface texture structure with most fibers in the CFF interleaf rooting in the fabrics benefits the improvement of the delamination resistance of the laminates. It is believed that the method was compatible with large scale manufacturing processes for CFRP laminate composites, and could find its real applications with the balance and compromising of toughness and in-plane tensile properties of the composites.

At last, a dopamine functionalization method was proposed to give a PDA layer on the CF surface. ZnO nanowires were then grafted on the PDA-modified CF through a hydrothermal method to obtain a hierarchical ZnO nanowire/carbon fiber composites. In situ pull-off experiments of a single ZnO NW from the CF demonstrated that the PDA functionalization on the fiber surface was critical for the strong chemical adhesion of the ZnO nanowires with the CF substrate caused by the coordination reaction between the catechol groups and  $Zn^{2+}$  ion, which yielded a 200% increase in pull-off force and adhesion strength compared to bare CF/ZnO NWs. The interfacial shear strength was also increased by 64% after the growth of ZnO NWs on the PDA-modified CF. It was noteworthy that PDA modification and ZnO NWs growth did not degrade the CF strength. Furthermore, both mode I and mode II interlaminar toughness were increased for CF/ZnO NWs and CF/PDA/ZnO NWs. In particular, for the latter laminates, the improvements were 63% for mode I and 22% for mode II due to the strong chemical bonding between PDA-modified CF and ZnO NWs as well as the mechanical interlocking between ZnO NWs and epoxy.

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