Research Article

Yonglyu He[#], Su Ju[#], Ke Duan, Jun Tang, Shuxin Bai, Dazhi Jiang^{*}, Yingying Pei and Jianwei Zhang^{*}

Tuning the through-thickness orientation of 1D nanocarbons to enhance the electrical conductivity and ILSS of hierarchical CFRP composites

<https://doi.org/10.1515/secm-2021-0040>
received April 21, 2021; accepted July 05, 2021

Abstract: In this article, we proposed a novel but simple multilayer resin film infusion-compressive molding (MLRFI-CM) manufacturing process that can harness the resin shear flow to architect hierarchical carbon fiber reinforced polymer (CFRP) composites with tunable 1D nanocarbons orientation. Via this novel process, we demonstrated that the orientation of two typical 1D nanocarbons, namely, the carbon nanotubes (CNTs) and carbon nanofibers (CNFs), can be successfully tuned via altering the infusion time and that the tuning strategy is especially effective toward CNTs. Further, the structure-performance relationships between the electrical conductivity/interlaminar shear strength (ILSS) and filler through-thickness orientation of the hierarchical CFRP composites is explored and compared. In the best case, with only 0.3 wt% of CNTs, the ILSS of CFRP composites revealed an

increase of 19.7%, and the through-thickness conductivity demonstrated an increase of 38%.

Key words: orientation tuning, electrical conductivity, ILSS

1 Introduction

Due to the lack of reinforcing carbon fiber in the interlaminar region, the electrical performance of CFRP laminates on through-thickness direction is limited by highly insulative (usually within $10^{-14} \sim 10^{-13}$ S/m) epoxy matrix. It poses challenges on the CFRP composites in the field of electrostatic protection and other structural-functional integrated applications such as electrothermal deicing [1,2] and composite health monitoring [3,4]. In addition, the long-standing “Achilles’ Heel” of laminated CFRP structures is the poor interlaminar mechanical property, also owing to the lack of interlaminar reinforcement. Therefore, introducing proper interlaminar reinforcements that can simultaneously enhance the through-thickness mechanical and electrical performance is of essential importance.

The most straightforward way is to introduce carbon fibers in the through-thickness direction. However, most of the common techniques (z-pin [5,6], fiber stitching [7,8], etc.) fail to reconcile the in-plane and through-thickness properties due to damaged fiber integrity or increased fiber-volume fraction resulting in the degradation of in-plane properties.

Since the discovery of 1D nanocarbons such as CNTs [9] and CNFs [10,11], hierarchical design down to the nanoscale of structural CFRP composite has become an alternative solution toward the aforementioned weakness of CFRP composite. The lengths and diameters of these nanocarbons are usually within a few microns and tens of nanometers, respectively. Hence, by introducing these

[#] This article is equally contributed by Yonglyu He and Su Ju.

*** Corresponding author: Dazhi Jiang**, Division of Advanced Composites Structures, School of Materials, Sun Yat-Sen University, 510006 Guangzhou, China, e-mail: jiangdzh@sysu.edu.cn

*** Corresponding author: Jianwei Zhang**, Department of Material Science and Engineering, College of Aerospace Science and Engineering, National University of Defense Technology, 410073 Changsha, China, e-mail: jwzhang.nudt@gmail.com

Yonglyu He, Su Ju, Jun Tang, Shuxin Bai: Department of Material Science and Engineering, College of Aerospace Science and Engineering, National University of Defense Technology, 410073 Changsha, China

Ke Duan: State Key Lab of Digital Manufacturing Equipment and Technology, School of Mechanical Science and Engineering, Huazhong University of Science and Technology, 430074 Wuhan, China

Yingying Pei: Department of Vacuum Technology, Shanghai Institute of Spacecraft Equipment, 200240 Shanghai, China

nanofillers into the composites, fiber integrity and volume fraction are not significantly influenced.

Both theoretical prediction [12] and experimental [13–15] results clearly suggest that the aligned 1D nanocarbons on the through-thickness direction can promote extra enhancements on the interlaminar mechanical properties and electrical conductivity as compared to nanocarbons with random orientation or in-plane orientation. For this reason, researchers have adopted a variety of approaches to appropriately introduce the nanofillers into the interlaminar region with preferential through-thickness alignment, for instance, vertically aligned array insertion [16–18], fiber surface growth [13,19–21], electric field alignment [14,15,22], magnetic field alignment [23], etc. However, the filler alignment achieved in the *ex situ* approaches like array insertion or fiber surface growth is often vulnerable to the fiber steric hindrance during composites forming, which may lead to degraded filler orientation and undesired bending/curving of the nanofillers [16,18,20,21]. *In situ* alignment approaches like electric/magnetic field alignment can alleviate the orientation degradation problem, but the application on the CFRP composites is rarely seen due to the lack of robustness during manufacturing, prolonged processing procedure, limitation of resin systems (only applicable to low viscosity resin systems) as well as associated safety issues (high electrical field).

Another *in situ* approach that harnesses resin shear flow to orientate the 1D nanofiller was explored in refs [24–27]. CNTs were successfully orientated along the through-thickness direction of FRP composites with the assistance of through-thickness resin flow. However, by comparing electric/magnetic field alignment approaches, how to precisely manipulate the CNT orientation was not realized in these approaches. The relationship between CNT through-thickness orientation and the mechanical and electrical performance of the composites was still absent. The effectiveness of the resin flow induced orientation on other 1D nanocarbons, for instance, CNF, with typical morphology not investigated. Moreover, regarding the quality of the composites fabricated with the reported approaches, the techniques were still immature with respect to fiber-volume fraction and voids content.

Therefore, in this article, we aim to innovate a multi-layer resin film infusion (MLRFI)-compressive molding (CM) process, with an attempt to precisely tune the orientation of two typical 1D nanocarbons, namely, CNTs and CNFs, along the CFRP through-thickness direction. Through this strategy, it's expected to build up hierarchical composites for simultaneously improving the interlaminar shear strength (ILSS) and electrical conductivity. Specifically, the effectiveness of tuning the CNTs/CNFs orientation

through the proposed MLRFI-CM process is first investigated and the corresponding orientation states of the nanocarbons are quantitatively characterized. Then, the effect of nanofiller orientation state on the through-thickness and transverse electrical conductivity and the corresponding mechanism is studied. Finally, the improvements in the composite ILSS resulting from varied orientations and types of the 1D nanocarbons are measured and compared.

2 Experimental

2.1 Materials

The carbon fiber fabrics applied in this work were 1k-T300 plain cloth and 6k-T700S-unidirectional fabric. The yarns of both fabrics were supplied by Toray Industry, Inc. The resin applied in this research was a modified aerospace grade epoxy with over 3.2 GPa tensile modulus and 90 MPa tensile strength. The soften temperature of this matrix system is 40°C. The viscosity of the resin system at 120°C is below 800 MPa and the gelation time at 120°C is over 15 min. The rheological characters provide the resin system with good processibility. The CNTs and the CNFs used in this research were supplied by *Times@nano Chengdu Organic Chemicals Co. Ltd* and fabricated by floating reactant method. The outer diameters of the CNTs and CNFs are in the range of 30–50 nm and 50–200 nm, respectively. The lengths of the CNTs and CNFs are in the range of 1–10 μm and 1–15 μm , respectively.

2.2 Strategy of tuning the CNTs/CNFs through-thickness orientation

According to the modeling studies in [24], the through-thickness orientation of the CNTs in the fiber nanochannels is increased under continuously applied through-thickness fluid field. Guided by this mechanism, the strategy of controlling the resin through-thickness infusion time during the composites forming to tune the CNTs/CNFs through-thickness orientation is proposed. However, it's usually technically difficult to control the infusion time during the composite forming, because under the vacuum pressure, the resin is continuously drained out until the resin is solidified. Controlling the infusion time by delaying the vacuum intervention or interrupting the resin infusion process would inevitably cause incomplete impregnation/poor densification.

For this reason, a joint MLRFI-CM process was proposed. Through the MLRFI process, the CNTs can be orientated in the through-thickness orientation, and by altering the infusion time, composites with different level of through-thickness alignment can be obtained. Once the infusion process is finished, the preform with aligned CNTs/CNFs was subjected to CM to cure and eliminate voids and to achieve desired fiber-volume content.

2.2.1 Joint MLRFI-CM process

In the conventional vacuum bag process [28–30], the vacuum bag is usually sealed with rubber tape which is highly viscous and sticky above 60°C. This character makes it difficult to remove the vacuum bag and the related auxiliary materials during the processing at relatively high temperature which prohibits the preform from being directly compressive molded after the infusion process. In addition, in conventional vacuum bagging, the size of the bagging film is usually 80–100% larger than the surface area of the preform in the purpose of creating deformation coordination zone to eliminate the air leakage induced by the film shrinkage (see Figure 1a). Consequently, the resin can still flow along the in-plane direction, which is unfavored when the resin flow needs to be precisely controlled as through-thickness flow.

Based on the above reasons, a self-sealing and deformation-controllable polydimethylsiloxane (PDMS) vacuum bag was designed and fabricated. Figure 1b demonstrates the self-sealing and controlled deformation characters of the as-proposed PDMS bag under vacuum pressure. After the external vacuum is applied, the relatively rigid wall of the PDMS bag can maintain the original dimensions, while the thinner roof on the upper surface of the vacuum bag shrinks and squeezes downwards under vacuum pressure, exerting a normal pressure on the preform. The animation form of the deformation process of the PDMS bag is given in Figure S1. With the aid of such PDMS bag, the resin flow within the preform can be strictly restricted to through-thickness direction. The specific details of the resin fluid field are schematically illustrated in Figure 1c.

To perform the MLRFI-CM process, partially impregnated preregs (PIP) preform was priorly prepared. PIP refers to a specially developed prepreg with rich resin content (up to 70 vol%) and only the bottom surface of the fabric was pre-impregnated shallowly by the resin film. The resin-rich design enables the preregs to generate sufficient resin flow during composite processing. The PIP preform was made by stacking multiple layers of PIP in sequence. 0.3 wt% CNTs and CNFs relative to resin mass were used to prepare the nanofiller-loaded resin film. Three-rolls-calendering process was adopted to disperse these carbon nanofillers. For specific details of

Figure 1: Schematics of the (a) conventional vacuum bag installation and the corresponding resin flow direction within the vacuum bags during processing. (b) The deformation process of the as-designed PDMS bag. (c) Deformation-controllable and self-sealing PDMS vacuum bag installation.

preparing PIPs and the nanofillers-loaded resin films, the audience can refer to our previous research [24].

The vacuum bag installation is shown in Figure 2b. To install the vacuum bag, the PIP preform, a layer of peer ply, and two layers of resin distribution medium (RDM) on the mold surface were laid in sequence. The highly permeable RDM was applied in the purpose of: (1) achieving relatively uniform vacuum pressure on the preform top surface; (2) creating a quasi-two-dimensional resin gathering space; and (3) quickly ducting out the resin accumulated on the top of the preform. The vacuum bag and a steel made coaming were then placed on the top of the RDM. The dimension of the PIP preform is roughly $200\text{ mm} \times 200\text{ mm} \times 8\text{ mm}$. The dimension of the inner-chamber of the undeformed bag is $205\text{ mm} \times 205\text{ mm} \times 12\text{ mm}$, which is slightly larger than the PIP preform. This ensures enough space for placing the peer ply and RDMs and for removing the vacuum bag readily without disturbing the preform once the through-thickness resin infusion is finished. The steel coaming was developed to increase the uniformity of the temperature field within the preform when the whole device was subject to the compressive molder for heating. This steel coaming could also provide 18.5 kPa normal pressure by its weight to anchor the vacuum bag for obtaining higher vacuum within the prepreg. Figure 2d shows the pressure variation of conventional rubber tape sealed vacuum

bag, PDMS vacuum bag, and PDMS bag with steel coaming, respectively, when the vacuum is continually applied. Figure 2e demonstrates the air leakage performance of the three different vacuum bag setups. According to Figure 2d and e, the PDMS bag with metal coaming demonstrates comparable vacuum level and air leakage performance with conventional rubber tape sealed vacuum bag.

The joint MLRFI-CM process is schematically illustrated in Figure 2a. This process consisted of three main procedures: (1) Preheating the preform to 120°C to melt the solid-state resin within the preform; (2) Applying the vacuum to generate through-thickness resin flow (Z-infusion) with desired time; and (3) Removing the vacuum device and compressively molding the composites to a designed thickness with the aid of thickness controllers and curing the composites under 2 MPa compressive pressure at 120°C for 2.5 h.

2.2.2 Laminate fabrication

CNTs- and CNFs-incorporated composites under varied Z-infusion time were prepared via the MLRFI-CM process. The temperature-viscosity profile of the composites would strongly influence the fiber-volume fraction and voids content of the final compressive molded composites. Hence, a

Figure 2: (a) The schematics of three main procedures of the MLRFI-CM processing. (b) The zoomed-in illustration of vacuum bag installation. (c) Photo of the processing device. (d) The absolute vacuum pressure variation. (e) Leakage performance of the different vacuum bag installation.

period of dwell time before CM was adopted. Since the incorporation of CNTs and CNFs showed very limited influence on the resin reactivity and viscosity (referring to Figure S2 in the supplementary information), the Z-infusion time of baseline, CNT, and CNF composites could be fixed as 0, 5, and 10 min, respectively. A total of 20 min processing time (vacuum infusion + dwell time) before CM was also fixed. The details with respect to the processing parameters, laminate thickness, and fiber-volume fractions of the as-prepared composites are given in Table 1.

2.3 Characterization

A TESCAN MAIA3 XMH scanning electron microscope (SEM) was employed to characterize the morphologies of the composites as well as the orientation of CNTs and CNFs. Prior to SEM observations, the samples were sputter-coated with platinum particles to enhance the image contrast. The transmission electrical microscope (TEM, Tecnai F30, FEI) was adopted to characterize the morphology and wall structures of the CNTs and CNFs applied in this research. Raman spectroscopy on the powder state CNT and CNF was performed on Renishaw Invia spectrophotometer using a 514 nm excitation wavelength and an acquisition range from 100 to 4,000/cm.

To measure the laminates' through-thickness and in-plane electrical conductivity, specimens were cut to dimensions of 15 mm × 15 mm × 2.45 mm and 15 mm × 5 mm × 2.45 mm, respectively, using water-jet cutting. The two-point-probe method which is commonly used for CFRP electrical measurement [31,32] was adopted, as the contact

resistance is relatively low with respect to the overall resistance. The conductivity tests were performed on a digital sourcemeter (Keithley 2450) to measure the electrical resistance between the two probes in the direction of interest. The corresponding surfaces were pre-coated with a thin layer of silver paint (Details of sample preparation are shown in Figure S3 in supplementary material) to guarantee that the electric current conducts uniformly along the measured direction and eliminate the influence of local contact resistance. A grid of five electrical resistance data was assessed on each specimen, and in each specimen set, three specimens were employed.

The DC conductivity σ is calculated according to the following equation (1).

$$\sigma = \frac{1}{\rho} = \frac{l}{R \times S}, \quad (1)$$

where ρ is the buck electrical resistivity, l is the length of the specimen along the direction of interest, and R is the resistance measured via the sourcemeter and S is the area of the plane perpendicular to the direction of interest.

The ILSS test was conducted in accordance with the ASTM D2344 standard using three-point bending mode with a constant loading speed of 1 mm/min. The applied load against the displacement of the specimen was recorded. The ILSS is calculated by equation (2).

$$\sigma_{\text{ILSS}} = 0.75 \times \frac{P_m}{b \times h}, \quad (2)$$

where, σ_{ILSS} is the ILSS (MPa), P_m is the maximum load obtained during the test (N), b is the specimen width (mm), and h is the specimen thickness (mm). In each experimental set, at least 5 specimens were employed.

Table 1: The molding parameters and fiber-volume fractions of the as-prepared composites

Composite label	*1CNT/CNF content (wt%)	Composite lay-up	Z-infusion time (min)	Dwell time before CM	Composite plate thickness (mm)	*3Fiber-volume fraction (Vol%)
Baseline-0 min	0	*2[WV ₂ UD ₆] _s	0	20	2.44	56.5
Baseline-10 min	0	[WV ₂ UD ₆] _s	10	10	2.45	55.3
CNT-0 min	0.3	[WV ₂ UD ₆] _s	0	20	2.44	55.1
CNT-5 min	0.3	[WV ₂ UD ₆] _s	5	15	2.45	54.8
CNT-10 min	0.3	[WV ₂ UD ₆] _s	10	10	2.46	54.7
CNF-0 min	0.3	[WV ₂ UD ₆] _s	0	20	2.47	54.5
CNF-5 min	0.3	[WV ₂ UD ₆] _s	5	15	2.46	55.6
CNT-10 min	0.3	[WV ₂ UD ₆] _s	10	10	2.46	54.9

*1CNT/CNF contents are related to the resin.

*2WV refers to the T300 1k plane-cloth woven fabric; UD refers to the T700 6k unidirectional fabric.

*3The fiber-volume fraction and voids content were calculated through the computer-assisted measurement of the composites' cross-sectional micro-photos using ImageJ. Each datum is the average datum picked from at least five different cross section area.

3 Results and discussion

3.1 CNT/CNF morphology and orientation

In order to better illustrate the structure-performance relation in the CNTs- and CNFs-incorporated composites, the morphologies of CNTs and CNFs as well as the dispersion state of CNTs and CNFs within the resin film applied in this research are characterized. Typical SEM and TEM micrographs are shown in Figure 3. Figure 3a–d compare the morphologies of the CNTs and CNFs. CNFs are remarkably straight compared to CNTs due to larger diameters and thicker walls. However, CNTs demonstrate irregular waviness and curving. By comparing Figure 3e and f which identify the molecular structures of CNTs and CNFs, CNTs exhibit uniform multiwall tubular structure consisting of sp^2 carbon, while CNFs show a combination of amorphous and cup-stacked sp^2 carbon. This is further

confirmed by the Raman spectra shown in Figure 3i. CNTs demonstrated higher value of I_D/I_G and much sharper G' band than that of CNFs, indicating the C atoms in the CNTs are more likely arranged in sp^2 state [33,34].

Figure 3g and h are SEM images that show the dispersion state of CNTs and CNFs in the original resin films. These two images clearly indicate that CNTs are better dispersed than CNFs within the as-prepared resin film.

Typical SEM images of CNT- and CNF-incorporated composites from edge view (observing direction is illustrated in Figure 4a) are shown in Figure 4. Figure 4b summarizes typical SEM images demonstrating the orientation state of CNTs and CNFs in the composites prepared under different processing parameters. In the CM solely processed composites (CNT-0 min and CNF-0 min), both CNTs and CNFs exhibit a certain level of in-plane orientation. This is mainly because the excessive resin tends to follow an in-plane flow when compressive pressure is

Figure 3: SEM images of the CNTs (a) and CNFs (b). TEM images of the CNTs (c) and CNFs (d); The molecular structures of typical CNT (e) and CNF (f). The SEM images illustrating the dispersion state of CNTs (g) and CNFs (h) within the resin film. (i) The Raman spectra of CNT and CNF.

Figure 4: (a) The schematic illustrating the viewing direction of the SEM images. (b) Typical SEM images demonstrating the orientation of CNTs/CNFs in the interlaminar region of the composites prepared under different processing parameters. (c) Schematics of the carbon fiber-posed steric hindrance effects on CNT and CNF.

solely applied, which drives the CNTs and CNFs in the resin to align along an in-plane orientation. After introducing the vacuum-assisted Z-infusion process before CM, the CNTs and CNFs in the composites demonstrate a certain level of orientation along the through-thickness direction in CNT-5 min, CNT-10 min, CNF-5 min, and CNF-10 min composites. By comparing the morphology of the CNTs in Figures 3 and 4, it can also be found that naturally wavy and curve CNTs are stretched by the through-thickness resin shear flow via the coordination of deformation when it passes through the fiber nanochannel (See Figure 4c).

To better compare and illustrate the nanofiller orientation, the orientation state of CNTs/CNFs is quantitatively measured. The orientation angle α of CNT/CNF along the thickness direction in the Y - Z plane (Figure 5a) is defined as the angle between CNT/CNF and the positive Y -axis. α (see Figure 5b) is measured as the angle between the line segment which starts from the lower end of the individual CNT/CNF to the upper end of this filler and the positive Y -axis. For each specimen set, at least 100 CNTs/CNFs are selected randomly from 20 to 30 SEM images with a consistent magnification of 10,000 $\times$. Note that, in both CNT-0 min and CNF-0 min specimens, few CNTs/CNFs

distributed in the Y - Z plane are found. Hence, the CNT-0 min and CNF-0 min composites are not summarized due to insufficient sample size. The statistical results of the orientation angle α are shown in Figure 5c-f, where the α is assumed to follow the Normal Distribution. The probability density function of normal distribution is given by equation (3).

$$f(\alpha) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(\alpha - \mu)^2}{2\sigma^2}\right), \quad (3)$$

where μ is the mathematical expectation of the orientation angle α , reflecting the mean orientation angle of the group of nanofillers. σ is the standard deviation of the measured orientation angle, which is an indicator of the uniformity of the group of CNTs/CNFs with respect to the major orientation angle.

The lower σ value implies the narrower the distribution of individual orientation angle, the higher the uniformity of the orientation state of the group of CNTs or CNFs.

According to the statistical analysis, the orientation state of the CNTs/CNFs in the composites processed under different Z-infusion times is compared. In the CNFs-incorporated composites, when the Z-infusion

Figure 5: The summary of typical SEM images demonstrating the distribution and orientation of CNTs/CNFs in the interlaminar region of the composites prepared under different Z-infusion times. (a) A schematic illustrating the orientation of CNT/CNF within the composites. (b) Illustration of measuring the orientation angle α . Statistical results of filler orientation angle in CNT-5 min (c), CNF-5 min (d), CNT-10 min (e), and CNF-10 min (f) composite, respectively.

time extends from 5 to 10 min, σ decreases indicating a higher orientation uniformity. In the composites containing CNTs, by extending the infusion time to 10 min, both the mean orientation angle and the orientation uniformity of CNTs drastically increased. The results clearly indicate that the proposed MLRFI-CM process can successfully tune the through-thickness orientation of the nanofillers. Additionally, by prolonging the vacuum-assisted Z-infusion time, the through-thickness orientation of both CNT and CNF can be further improved.

Furthermore, by comparing the σ and μ value of the CNT and CNF composites subjected to same Z-infusion process, the mean orientation angle and the orientation uniformity of CNT composites are significantly higher as compared to results in CNF composite. This implies that CNTs exhibit better ability of fluid-field-induced orientation than that of CNFs.

This can be explained by the schematic illustration shown in Figure 5c. The CNFs possess diameters around 50–200 nm, which approach the width of the nanochannels

between two neighbored carbon fibers (100–3,000 nm). However, the diameters of CNTs are usually below 50 nm. Hence, these nanochannels pose greater hindrance effect on the CNFs. Moreover, the typical interlaminar distance of the prepared composites is usually between 5 and 20 μm which is closer to the CNFs' length. Therefore, the steric hindrance effects induced from neighbored carbon fibers on the through-thickness orientation of the CNFs. Last, the bending stiffness of the nanofillers is proportional to the fourth power of the diameter of the nanofiller. As is confirmed by Figure 4, CNFs with higher diameter are remarkably rigid which makes it difficult for CNFs to pass through the nanochannel via deformation coordination during the Z-infusion process. In contrast, the CNTs have hollow structures, and the diameters are smaller than those of CNFs. When they encounter fiber hindrance, they are believed to exhibit better deformation coordination ability (Figure 5c). Hence, CNTs are more easily oriented with the assistance of resin flow.

3.2 Electrical conductivity characterization

The measured electrical conductivities on the through-thickness direction and the transverse direction of the composites under different Z-infusion time are summarized in Figure 6a and b, respectively. It can be observed in Figure 6a that the incorporation of 0.3 wt% CNFs and CNTs can effectively improve the through-thickness conductivity of the composite. And for both CNTs and CNFs composites, the electrical conductivity can be further improved by extending the Z-infusion time. This improvement is especially significant in the CNT composites. By prolonging the Z-infusion time from 5 to 10 min, the through-thickness conductivity of composite further increases from 5.64 to 6.65 S/m. Compared with the baseline-0 min specimen, the conductivity of CNT-5 min and CNT-10 min is increased by 17 and 38%, respectively. Correspondingly, composites with CNF incorporation demonstrate less obvious enhancement in the through-thickness conductivity. There are only insignificant enhancements of 7 and 9% in the conductivities for CNF-5 min and CNF-10 min, respectively.

Compared with CNFs, the higher efficiency of CNT in enhancing the composites' through-thickness conductivity is resulted from three reasons. First is the difference in intrinsic conductivity between CNT and CNF. It is confirmed in the Figure 3 that the C atoms of CNT are in the uniform sp^2 state. The high density of the π -electron cloud on CNT leads to better electron mobility. However, in the CNF molecules, obvious amorphous carbons are observed in the outer wall, leading to poor electron

mobility. The sp^2 state carbon in the CNF inner walls is also observed. But these carbon atoms are arranged in cup-stack form which is not favorable for electron transport [35,36]. Second, based on the aforementioned discussion, it is identified that CNTs within the composites have higher degree of orientation in the through-thickness direction. Therefore, the conductive network bridging the nearby lamina is more likely to form. Third, the volume of individual CNT is remarkably smaller than that of individual CNF and the CNTs demonstrate better dispersion state in the matrix. Hence, under the same mass fraction, the number and specific surface area of CNTs are both significantly higher than those of CNFs, resulting in more sufficient number of conductive paths. Conclusively, CNTs are more effective in improving the conductivity of composite than CNFs.

The transverse (perpendicular to fiber direction) conductivity of the baseline and CNTs/CNFs-incorporated composites are further analyzed in the purpose of better illustrating the orientation characteristics of CNTs/CNFs within the composites. According to Figure 6b, by extending the Z-infusion time, the transverse conductivities of both CNT and CNF composites demonstrate a tendency from climbing to slipping. The CNT and CNF composites under 5 min Z-infusion demonstrate the highest transverse conductivities. This tendency is assumed to be induced by the change of filler orientation within the composite. As is schematically illustrated in Figure 7, both nanofillers undergo 5 min through-thickness infusion and exhibit a medium level of through-thickness orientation. Consequently, they are capable of bridging the neighbored off-plane fibers forming more

Figure 6: (a) The through-thickness conductivity and (b) the transverse conductivity of the baseline and CNTs/CNFs-incorporated composites under different Z-infusion times.

Figure 7: Schematics of through-thickness conductive paths (a)–(c) and in-plane conductive paths (d)–(f) within the composites with varied orientation state of the nanofillers. (g) Typical optical images of the cross section from the CNT-10 min composite and the zoom-in image (h).

conductive paths in both through-thickness and transverse direction. However, by further prolonging the impregnation time to 10 min, the bridging effects on the transverse direction are undermined because the component of the nanofiller orientation in the X direction is further reduced, thereby weakening the bridging effect in the in-plane direction. By studying the variation trend of transverse conductivity of the composites under varied Z -infusion time, the corresponding filler orientations are further revealed. This further proves the effectiveness of tuning the filler orientation via as-proposed MLRFI-CM procedure.

In conclusion, the highly insulated epoxy within the composite interlaminar region plays a dominant role in deteriorating the conductivity of the composite in the through-thickness direction (see Figure 7g). By bridging the upper and lower lamina, the Z -aligned CNTs/CNFs can form conductive paths in the through-thickness direction,

thereby greatly improving the conductivity along Z -direction. Admittedly, the contribution of CNTs/CNFs to the transverse conductivity is limited in that changing the distribution and orientation of these highly conductive nanocarbons within the composites does not alter the conduction mechanism, that is, fibers contacted with neighbored fibers on their radical direction form the major conductive network (referring to orange curve in Figure 7h).

3.3 Characterization of the composite ILSS

Figure 8 summarizes the ILSS results of baseline and CNTs/CNFs-incorporated composites under different Z -infusion times. As the vacuum-assisted impregnation time increases from 0 to 10 min, ILSS of the CNF composites increases slightly from 51.42 to 53.65 MPa by 4.3%.

Figure 8: (a) The test results of baseline and CNTs/CNFs-incorporated composites under different z-infusion processing times. (b) Typical interlaminar shear load-displacement curves. (c) The schematical illustration of the enhancing mechanism of the 1D nanocarbons. The tensile fractured surface of CNFs (d) and CNTs (e)-incorporated epoxy nanocomposites.

Correspondingly, for the CNTs-loaded composites, the ILSS increased by 6.1 and 12.4%, respectively, when the vacuum-infusion time prolongs to 5 and 10 min. Compared with the baseline composite, the ILSS of CNT-10 min composites is increased most significantly by 19.7% (from 50.43 to 60.38 MPa). Conclusively, for CNTs/CNFs-incorporated composites, the ILSS can be effectively increased by prolonging the vacuum-assisted infusion time.

It is well-established that [16,37,38] when CNTs/CNFs are sufficiently and effectively oriented along the thickness direction and stitching into the interfiber space, these CNTs/CNFs can play a role in altering the distribution of interlaminar shear stress and enhance the ILSS. By referring to the typical Load-displacement curves shown in Figure 8b, it is noticed that by increasing the CNT/CNF through-thickness orientation, the higher damage initiation resistance is observed owing to the micro-crack anchoring and arresting of the Z-orientated fillers (schematically illustrated in Figure 8c). The enhanced crack

propagation resistance is also observed in Figure 8b due to the fact that the highly orientated nanofillers in through-thickness direction can effectively deflect and bridge the cracks. On the contrary, the in-plane orientated nanofillers can hardly “pin” the micro-cracks, nor can it provide sufficient deflecting/bridging effects toward the main crack.

Additionally, enhancements of CNTs and CNFs are compared. It's found that the CNTs demonstrated superior enhancing effects on the composite ILSS. It is mainly due to four reasons: (1) higher through-thickness orientation, (2) superior intrinsic mechanical properties, (3) more homogenous dispersion, and (4) better interfacial bonding with the epoxy matrix.

Figure 8d and e compare the tensile-fractured surface of the CNT and CNF-incorporated nanocomposites. As is marked by the yellow arrow in Figure 8d, the interfacial space between CNFs and epoxy matrix formed after the tensile failure indicates poor interfacial bonding between the CNF and matrix. However, on the fracture surface of

CNTs-loaded specimen (Figure 8e), very limited CNT/matrix interfacial space is observed. Moreover, through comparing the CNTs/CNFs highlighted by the orange color, CNTs demonstrated rough and epoxy-attached surface, while the surface of the CNFs is smooth without epoxy attachment. This also reveals that CNF has poorer bonding properties with the matrix compared to those of CNT.

4 Conclusion

In this article, a simple and novel MLRFI-CM composites forming process based on a self-sealing and deformation-controllable vacuum bag is proposed to harness the resin shear flow to architect CFRP composites with hierarchically arranged 1D nanocarbons, namely, CNTs and CNFs. Via the construction of such hierarchical CFRP composites, the feasibility of simultaneously enhancing the CFRP electrical conductivity and ILSS is obtained. Based on the experimental results, several conclusions are made as follows:

- (1) Through the proposed MLRFI-CM process, the through-thickness orientation of CNTs and CNFs can be successfully tuned. The extension of the resin infusion time induces higher through-thickness orientation. This strategy is especially effective toward CNTs in that the interfiber nanochannels pose smaller steric hindrance on thinner and shorter CNTs than CNFs and that the deformation coordination ability of CNTs is better. Moreover, the straightening phenomenon of naturally wavy and curved CNTs is also evident when employing the Z-infusion. This phenomenon is believed to be induced by deformation coordination when CNTs pass through the interfiber nanochannels. In summary, the proposed tuning strategy provides a simple and effective tool in manipulating the orientation of 1D nano-reinforcements in the field of hierarchical FRP composites.
- (2) Via the proposed process, the hierarchical composites with the addition of 0.3 wt% CNTs and CNFs all demonstrate improved through-thickness electrical conductivity and ILSS simultaneously. The composites processed through longer Z-infusion time demonstrate higher through-thickness electrical conductivity and ILSS, among which the CNT-10 min composite exhibited the most remarkable increase in both the through-thickness conductivity by 38% and the ILSS by 19.7%. From the perspective of structure-performance relationship, the tendency of both the electrical conductivities

and ILSS by varying the Z-infusion time is also a reflection of the effectiveness of tuning the orientation of 1D nanocarbons via the as-proposed MLRFI-CM forming process.

Funding information: The authors acknowledge financial support from National Natural Science Foundation of China with grant No. 51803236, No. 51803122, and No. 52003295.

Conflict of interest: Authors state no conflict of interest.

Reference

- [1] Vertuccio L, De Santis F, Pantani R, Lafdi K, Guadagno L. Effective de-icing skin using graphene-based flexible heater. *Compos Part B Eng.* 2019;162:600–10.
- [2] Yao X, Falzon BG, Hawkins SC, Tsantalis S. Aligned carbon nanotube webs embedded in a composite laminate: a route towards a highly tunable electro-thermal system. *Carbon N Y.* 2018;129:486–94.
- [3] Rein MD, Breuer O, Wagner HD. Sensors and sensitivity: carbon nanotube buckypaper films as strain sensing devices. *Compos Sci Technol.* 2011;71:373–81.
- [4] Irfan MS, Khan T, Hussain T, Liao K, Umer R. Carbon coated piezoresistive fiber sensors: from process monitoring to structural health monitoring of composites – A review. *Compos Part A Appl Sci Manuf.* 2021;141:106236.
- [5] Grassi M, Zhang X, Meo M. Prediction of stiffness and stresses in z-fibre reinforced composite laminates. *Compos Part A Appl Sci Manuf.* 2002;33:1653–64.
- [6] Chang P, Mouritz AP, Cox BN. Properties and failure mechanisms of pinned composite lap joints in monotonic and cyclic tension. *Compos Sci Technol.* 2006;66:2163–76.
- [7] Lomov SV, Belov EB, Bischoff T, Ghosh SB, Truong Chi T, Verpoest I. Carbon composites based on multiaxial multiply stitched preforms. Part 1. Geometry of the preform. *Compos Part A Appl Sci Manuf.* 2002;33:1171–83.
- [8] Barile C, Casavola C, Pappalettere C. The influence of stitching and unconventional fibres orientation on the tensile properties of CFRP laminates. *Compos Part B Eng.* 2017;110:248–54.
- [9] Iijima S. Helical microtubules of graphitic carbon. *Nature.* 1991;354:56–8.
- [10] De Jong KP, Geus JW. Carbon Nanofibers: catalytic Synthesis and Applications. *Catal Rev - Sci Eng.* 2000;42:481–510.
- [11] Al-Saleh MH, Sundararaj U. A review of vapor grown carbon nanofiber/polymer conductive composites. *Carbon N Y.* 2009;47:2–22.
- [12] Menna C, Bakis CE, Prota A. Effect of nanofiller length and orientation distributions on Mode I fracture toughness of unidirectional fiber composites. *J Compos Mater.* 2016;50:1331–52.
- [13] Lv P, Feng Y, Zhang P, Chen H, Zhao N, Feng W. Increasing the interfacial strength in carbon fiber/epoxy composites by controlling the orientation and length of carbon nanotubes grown on the fibers. *Carbon N Y.* 2011;49:4665–73.
- [14] Ladani RB, Wu S, Kinloch AJ, Ghorbani K, Zhang J, Mouritz AP, et al. Multifunctional properties of epoxy nanocomposites

- reinforced by aligned nanoscale carbon. *Mater Des.* 2016;94:554–64.
- [15] Ravindran AR, Ladani RB, Wu S, Kinloch AJ, Wang CH, Mouritz AP. Multi-scale toughening of epoxy composites via electric field alignment of carbon nanofibres and short carbon fibres. *Compos Sci Technol.* 2018;167:115–25.
- [16] Kalfon-Cohen E, Kopp R, Furtado C, Ni X, Arteiro A, Borstnar G, et al. Synergetic effects of thin plies and aligned carbon nanotube interlaminar reinforcement in composite laminates. *Compos Sci Technol.* 2018;166:160–8.
- [17] Garcia EJ, Wardle BL, John Hart A. Joining prepreg composite interfaces with aligned carbon nanotubes. *Compos Part A Appl Sci Manuf.* 2008;39:1065–70.
- [18] Ni X, Furtado C, Kalfon-Cohen E, Zhou Y, Valdes GA, Hank TJ, et al. Static and fatigue interlaminar shear reinforcement in aligned carbon nanotube-reinforced hierarchical advanced composites. *Compos Part A Appl Sci Manuf.* 2019;120:106–15.
- [19] Zakaria MR, Md Akil H, Abdul Kudus MH, Ullah F, Javed F, Nosbi N. Hybrid carbon fiber-carbon nanotubes reinforced polymer composites: a review. *Compos Part B Eng.* 2019;176:107313.
- [20] Wicks SS, Wang W, Williams MR, Wardle BL. Multi-scale interlaminar fracture mechanisms in woven composite laminates reinforced with aligned carbon nanotubes. *Compos Sci Technol.* 2014;100:128–35.
- [21] Li R, Lachman N, Florin P, Wagner HD, Wardle BL. Hierarchical carbon nanotube carbon fiber unidirectional composites with preserved tensile and interfacial properties. *Compos Sci Technol.* 2015;117:139–45.
- [22] Ladani RB, Wu S, Kinloch AJ, Ghorbani K, Zhang J, Mouritz AP, et al. Improving the toughness and electrical conductivity of epoxy nanocomposites by using aligned carbon nanofibres. *Compos Sci Technol.* 2015;117:146–58.
- [23] Wu S, Ladani RB, Zhang J, Kinloch AJ, Zhao Z, Ma J, et al. Epoxy nanocomposites containing magnetite-carbon nanofibers aligned using a weak magnetic field. *Polymer (Guildf).* 2015;68:25–34.
- [24] He Y, Zhang J, Yao L, Tang J, Che B, Ju S, et al. A multi-layer resin film infusion process to control CNTs distribution and alignment for improving CFRP interlaminar fracture toughness. *Compos Struct.* 2021;260:113510.
- [25] Kirmse S, Ranabhat B, Hsiao KT. Experimental and analytical investigation on the interlaminar shear strength of carbon fiber composites reinforced with carbon nanofiber z-threads. *Mater Today Commun.* 2020;25:101512.
- [26] Fan Z, Santare MH, Advani SG. Interlaminar shear strength of glass fiber reinforced epoxy composites enhanced with multi-walled carbon nanotubes. *Compos Part A Appl Sci Manuf.* 2008;39:540–54.
- [27] Yokozeki T, Iwahori Y, Ishibashi M, Yanagisawa T, Imai K, Arai M, et al. Fracture toughness improvement of CFRP laminates by dispersion of cup-stacked carbon nanotubes. *Compos Sci Technol.* 2009;69:2268–73.
- [28] Qi B, Raju J, Kruckenberg T, Stanning R. A resin film infusion process for manufacture of advanced composite structures. *Compos Struct.* 1999;47:471–6.
- [29] Stringer LG. Optimization of the wet lay-up/vacuum bag process for the fabrication of carbon fibre epoxy composites with high fibre fraction and low void content. *Composites.* 1989;20:441–52.
- [30] Wang B, Duan Y, Xin Z, Yao X, Abliz D, Ziegmann G. Fabrication of an enriched graphene surface protection of carbon fiber/epoxy composites for lightning strike via a percolating-assisted resin film infusion method. *Compos Sci Technol.* 2018;158:51–60.
- [31] Kandare E, Khatibi AA, Yoo S, Wang R, Ma J, Olivier P, et al. Improving the through-thickness thermal and electrical conductivity of carbon fibre/epoxy laminates by exploiting synergy between graphene and silver nano-inclusions. *Compos Part A Appl Sci Manuf.* 2015;69:72–82.
- [32] Qin W, Vautard F, Drzal LT, Yu J. Mechanical and electrical properties of carbon fiber composites with incorporation of graphene nanoplatelets at the fiber-matrix interphase. *Compos Part B Eng.* 2015;69:335–41.
- [33] Chuang CC, Huang JH, Chen WJ, Lee CC, Chang YY. Role of amorphous carbon nanowires in reducing the turn-on field of carbon films prepared by microwave-heated CVD. *Diam Relat Mater.* 2004;13:1012–6.
- [34] DiLeo RA, Landi BJ, Raffaele RP. Purity assessment of multi-walled carbon nanotubes by Raman spectroscopy. *J Appl Phys.* 2007;101:101.
- [35] Endo M, Kim YA, Hayashi T, Nishimura K, Matusita T, Miyashita K, et al. Vapor-grown carbon fibers (VGCf) – Basic properties and their battery applications. *Carbon N Y.* 2001;39:1287–97.
- [36] Endo M, Kim YA, Hayashi T, Fukai Y, Oshida K, Terrones M, et al. Structural characterization of cup-stacked-type nanofibers with an entirely hollow core. *Appl Phys Lett.* 2002;80:1267–9.
- [37] Liu Q, Lomov SV, Gorbatiikh L. When does nanotube grafting on fibers benefit the strength and toughness of composites? *Compos Sci Technol.* 2020;188:107989.
- [38] Romanov VS, Lomov SV, Verpoest I, Gorbatiikh L. Can carbon nanotubes grown on fibers fundamentally change stress distribution in a composite. *Compos Part A Appl Sci Manuf.* 2014;63:32–4.