The effect of carbon nanotubes wrapping conformation on the interfacial properties of carbon fiber

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Abstract

In order to realize the goal of mass production of modification technology, CNTs would be dispersed in gas phase rapidly and then be sprayed to the surface of industrial CF that contain sizing agent. This will increase Interface shear strength (IFSS) of CF from 26MPa before processing to 35MPa maximum (increased about 33.9%). Due to the embedding function that sizing agent has on CNTs, three types of CNTs adhering to the surface of CF are formed. They are complete embedding type ($\sigma_1$), partial embedding type ($\sigma_2$) and sufficient exposure type ($\sigma_3$). This paper analyses the relations between three formations and processing time, and the contribution to IFSS of each type. It is found that the low content of $\sigma_1$ has a positive effect on IFSS which can reach 6MPa and $\sigma_2$ has an even stronger effect on the improvement of IFSS compared with $\sigma_1$ on the same concentration. While $\sigma_3$ has a negative effect on IFSS all the time.

1. Introduction

Carbon fiber resin composite (CFRP) is widely used in fields of aviation and transportation because of its excellent specific strength [1]. However, the smooth surface and the low chemical reactivity make interfacial bonding between CF and matrix resin weak, which greatly decreases the stress transfer of CFRP [2]. CNTs’ outstanding mechanical properties and nanoscale morphological characteristics make it a material that is extensively adopted and studied in the interface enhancement subject of CFRP [3]. The mechanical interlock effect by putting CNTs into the surface of CFRP can greatly enhance the interfacial property of composite materials. This is widely verified [4–9]. The main methods are: chemical vapor deposition (CVD) [4,13] electrophoretic deposition (EPD) [11,12], chemical functionalization [14,15], coating of fibers with CNT-containing sizing and etc. CF needs to embed into the sizing agent in production so that polymer coating would form on the surface of CF [18]. The polymer coating not only can prevent the fiber damage and be easy to process, but also make up for the fiber surface defects, increase fiber surface energy and improve stress transfer efficiency [17–21]. Therefore, there are only a few ways among the introduction of CNTs suitable for the actual production (most of the commercial CF needs to be desized), of which the limit of technology makes the modification effect that CNTs has on CFRP. For example, Liu et al. modified CF in the way of embedding CF into MWCNTs-COOH suspension liquid, IFSS just increased about 9.8% [22]. While Cao et al. used sizing agent that mixed CNTs, epoxy, Tween-80 and Span-60 to modify CF, IFSS only increased 14.7% [23].

To adjust to the existence of sizing agent on the surface of CF as soon as possible. In this paper, a gas-phase dispersion and spraying method of CNTs based on plasma thermal excitation is proposed, in which CNTs dispersed in the gas-phase space are directly adhered to the CF surface with the help of sizing agent without any pretreatment of commercial CF, thus enabling CNTs to play an active role in the CFRP interface. Due to the intervention of sizing agent, there are actually two CFRP interfaces: CF-sizing agent and sizing agent-resin. The introduction of gas-phase CNTs work together with sizing agent and resin and form three structures in the perspective of interface: complete embedding type ($\sigma_1$, Fig. 1(a)), partial embedding type ($\sigma_2$, Fig. 1(b)) and sufficient exposure type ($\sigma_3$, Fig. 1(c)). $\sigma_1$’s contribution comes
from the increase of roughness on sizing agent-resin interface [24]. \( \sigma_2 \)'s contribution derives from the cross-interface shearing effect on sizing agent-[25]-resin interface. And \( \sigma_3 \) completely embeds in resin and plays an uncertain role in interface enhancement [26]. This paper finds out the formation rule of \( \sigma_1 \)-\( \sigma_3 \) in the process of experiment and studies the contribution to IFSS of these three types respectively, providing a fundamental reference to the integration of present technology and modified technology.

2. Experimental

2.1. Materials

Carbon fiber monofilament (taken from carbon fiber filament T700SC, Zhongfu Shenying CF co. Ltd., Lianyungang, Jiangsu, China), with a cross-section diameter of 6.7–7.3µm and a sizing content of 1%.

MWCNTs (GT-300; Shandong Dazhan Nano Materials co.Ltd., China; length, 15–30µm; diameter, 5–15nm).

\( \text{H}_2\text{O} \): Deionized water (DI water).

Sizing agent (Zhongfu Shenying CF co. Ltd., Lianyungang, Jiangsu, China).

Resin and curing agent (MF-4101H, ZH-520, Hubei Zhen Zhengfeng Advanced Materials co. Ltd.).

2.2. Method and equipment

(b) the process of purging.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Experimental variable:</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>25 mm/s</td>
</tr>
<tr>
<td>S0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25 mm/s</td>
</tr>
<tr>
<td>S1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25 mm/s</td>
</tr>
<tr>
<td>S2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25 mm/s</td>
</tr>
<tr>
<td>S3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>16.6 mm/s</td>
</tr>
<tr>
<td>S4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.5 mm/s</td>
</tr>
<tr>
<td>S5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10 mm/s</td>
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<table>
<thead>
<tr>
<th>Variable conversion:</th>
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<tbody>
<tr>
<td>Deposition time(t)</td>
</tr>
<tr>
<td>1.6s</td>
</tr>
<tr>
<td>0.8s</td>
</tr>
<tr>
<td>1.6s</td>
</tr>
<tr>
<td>2.4s</td>
</tr>
<tr>
<td>3.2s</td>
</tr>
<tr>
<td>4.0s</td>
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</table>

<table>
<thead>
<tr>
<th>Spray object</th>
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</thead>
<tbody>
<tr>
<td>Si wafer</td>
</tr>
<tr>
<td>CF</td>
</tr>
<tr>
<td>CF</td>
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<td>CF</td>
</tr>
<tr>
<td>CF</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Other parameters</th>
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<tbody>
<tr>
<td>CF length: 40mm</td>
</tr>
<tr>
<td>Electrode voltage: 10KV</td>
</tr>
<tr>
<td>Distance between electrodes: 0.5mm</td>
</tr>
</tbody>
</table>

As shown in Fig. 2(a), please refer to the gas phase dispersion method of CNTs reported by Li et al [27–30]. CNTs gas phase spray was made by self-made equipment. In the coaxial electrodes, the inner
electrode is made of a mixture of CNTs and deionized water as the negative electrode, and the outer electrode is composed of an empty-cup-shaped electrode with a hole as the positive electrode. The two electrodes generate a 10KV voltage after connecting the power. Then 1bar compressed air is injected between the electrodes, serving as the plasma actuating medium. Thus, a controllable power plasma arc is generated near the electrode top, which leads to a drastic layer-by-layer dispersion of the mixed electrode of CNTs. After dispersion, free CNTs are ejected from the positive electrode hole driven by compressed air. CNTs move and diffuse further under the inertia effect, and adhere to each other under the effect of Van der Waals forces when they encounter the front CF monofilaments. CF monofilaments were uniformly coated on one side through linear movement. Then samples were reversed and the above operation was performed again to coat the outer circumferences with CNTs. The specific parameters are listed in Table 1. Then bake samples for 10 minutes at 80°C and cool them down. Soften sizing agent and then set the shape. Note the resulting sample as S1-S5. To get the total adhesion quantity of CNTs (even no difference among σ1, σ2 and σ3), Si wafer would be spayed with the same technology and noted as S0. In order to explore the adhesion situation of CNTs on the surface of CF and to remove CNTs that lack of bond, S1-S5 (double sides) were purged by room-temperature compressed air as illustrated in Fig. 2(b). Naming for samples is shown in Table 2.

<table>
<thead>
<tr>
<th>Flow rate (m/s)</th>
<th>0</th>
<th>0.4</th>
<th>0.8</th>
<th>1.2</th>
<th>1.6</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample name</td>
<td>Sx</td>
<td>Sxa</td>
<td>Sxb</td>
<td>Sxc</td>
<td>Sxd</td>
<td>Sxe</td>
</tr>
</tbody>
</table>

### 2.3. Conversion processing of σ2 to σ1

In Fig. 3, surface tension of liquid of ethyl alcohol was used to make the uncovering part of σ2 tightly stick to the surface of CF, turning all σ2 into σ1 in order to study σ1’s and σ2’s contribution to interfacial mechanical properties respectively. The specific steps are as follows: put S1e-S5e samples into ethanol solution for 2 seconds and then take them out and drain them off. Bake the samples for 10 minutes at 80°C and cool them down. Note those samples as S1e′-S5e′.

### 2.4. Morphology characterization

Field emission scanning electron microscope (SEM) (SU-8010; Hitachi, Tokyo, Japan) was used to characterize the CNTs distribution on the surface of F.

As shown in Fig. 4, microscopic image method [31] was used to quantitatively characterize the concentration of CNTs on the CF surface. One observation point was randomly selected every 100µm right above CF to obtain SEM photos and digitally process photos by an image processing software named Image J, with a total of 40 observation points per sample. The general rule of SEM and material imaging is as follows: CNTs will be embedded to a certain extent due to sizing agent on the surface of CF. The feedback signal of embedded CNTs is weak because of the charge effect of electron accumulation.
While the feedback signal of unembedded CNTs is strong due to the sufficient amount of secondary electrons, as shown in Table 3.

<table>
<thead>
<tr>
<th>Surface material</th>
<th>Sizing agent</th>
<th>CNTs</th>
<th>CF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corresponding structure</td>
<td>Consistent/σ1/σ2(fractional)</td>
<td>σ2(fractional)/σ3</td>
<td>Consistent</td>
</tr>
<tr>
<td>Signal intensity</td>
<td>Weak</td>
<td>Strong</td>
<td>Strong</td>
</tr>
</tbody>
</table>

Table 3

The associative architecture of different materials and signal feedback.

The coverage ratio C of CNTs on the surface of CF is as follows: \[ C = \frac{S_C}{S} \times 100\%, \] where \( S_C \) is the accumulated area of CNTs recognized by signal, \( S \) is the total area of the randomly selected images.

The coverage ratio of \( \sigma_1, \sigma_2 \) and \( \sigma_3 \) can be calculated by equations:

\[
\begin{align*}
C_T &= C_\delta + C_\epsilon + C_\gamma \\
C_U &= \beta C_\epsilon + C_\gamma \\
C_\gamma &= C_U - C_V
\end{align*}
\]

where \( C_T \) is the total coverage ratio of samples without sizing agent, \( C_\delta \) is the coverage ratio of \( \sigma_1 \), \( C_\epsilon \) is the coverage ratio of \( \sigma_2 \), \( C_\gamma \) is the coverage ratio of \( \sigma_3 \), \( C_U \) is the coverage ratio without being purged, \( C_V \) is the coverage ratio after being purged by 2.0m/s airflow (the strongest airflow, ensuring that all \( \sigma_3 \) is removed), \( \beta \) is the signal recognition constant of \( \sigma_2 \), which is \( \frac{3}{5} \).

2.5. The interfacial shear strength test of CFs

Microdroplet test [32] was used to test IFSS performance of CF monofilament. A microsyringe was used to adhere the CF monofilament in the form of one or more discrete resin microdroplets (curing time \( t_1 = 15 \text{min}, t_2 = 15 \text{min}, \) curing temperature \( T_1 = 150^\circ C, T_2 = 180^\circ C \)). Under the microscope, resin balls with a diameter of less than 0.2mm were selected for pull-out test. CF peeled resin balls between micro vice blades at a speed of 1um/s, and the mechanical sensor collected CF stress strength in real time.

Assuming that the axial interfacial shear stress of CF is constant [33], IFSS can be calculated by equation [34]:\[ \tau = \frac{F}{\pi DL}, \] where \( \tau \) is the interfacial shear strength (IFSS), \( F \) is the maximum pull out force, \( D \) is the fiber diameter. And \( L \) is the micro-droplet embedding length, ranging from 50–70µm. The effective data amount of each sample was 40–50[34].

3. Results And Discussion

3.1. Surface microscopic characterization

As shown in Fig. 5, highly dispersed CNTs gradually accumulated on the surface of CF with the increase of CNTs processing time. Within the shortest processing time, \( \sigma_1 \) and \( \sigma_2 \) could coexist, which is due to
the fluidity of the sizing agent softened at high temperature and the good wettability between CNTs and sizing agent, enabling the embedding of CNTs by sizing agent. When \( t = 2.4s \), \( \sigma_3 \) started to come into being. When \( t = 2.4-4.0s \), \( \sigma_3 \) developed rapidly. The irregular shapes caused by defects of CNTs made it randomly for \( \sigma_1 \) and \( \sigma_2 \) to come into being. For this reason, \( \sigma_1 \) and \( \sigma_2 \) generate synchronously. Obviously, the shorter the CNTs are, the less irregular the shapes will be. And it will be easier for \( \sigma_1 \) to come into being on the surface of CF. As Fig. 5 shows, the exposure parts of \( \sigma_2 \) interfered with subsequent CNTs through Van der Waals’ force. Therefore, it is even harder for CNTs hanged by the exposure parts of \( \sigma_2 \) to be embedded into sizing agent, which leads to the result that only \( \sigma_3 \) and slightly-embedded \( \sigma_2 \) generated. Hence, with the increase of the processing time, it is hard for \( \sigma_2 \)’s density to increase continuously. Instead, \( \sigma_3 \)’s density continued to increase and only \( \sigma_3 \) were formed.

It can be seen from 5b that airflow purging has a significant effect on removing CNTs on the surface of CF. Compared 5(a) with (b), when \( t = 0.8s \), samples had no obvious change before and after purging. This is because this group of samples only contained \( \sigma_1 \) and \( \sigma_2 \). And due to the embedding effect of sizing agent, these two types of CNTs were barely affected by airflow. While the amount of CNTs decreased clearly in samples S2e, S3e, S4e and S5e when \( t = 1.6-4.0s \). And the overall content of CNTs in 5 samples in Fig. 5(b) was similar, indicating that \( \sigma_3 \) was susceptible to airflow of various velocities and can be completely removed.

As Fig. 6 shows, a large area of residual CNTs and resin balls can be seen from the fracture surface. By observing the CF surface at a higher resolution, as shown by the short arrow in Fig. 6, residues of CNTs can be found on the CF surface. In addition, pores remained in the resin on the CF surface after CNTs were striped, as shown in the oval area. Rough surfaces and residual CNTs mean that bond failure will occur between the CNTs layer and the epoxy of the composite, indicating a significant improvement in interface adhesion. But there is no large area of exposed CF, which means sizing agent-CF interface is significantly better than sizing agent-resin interface. This is in line with the present study conclusion [35]. Also, it indicates that only sizing agent-resin interface is involved in all studies and the interference from sizing agent-CF interface can be excluded in the discussion of mechanical contributions of \( \sigma_1 \), \( \sigma_2 \) and \( \sigma_3 \).

### 3.2. Quantitative analysis using microscopic image method

As pictured in Fig. 7, the CNTs content decreased with the increase of the purging airflow during the same processing time, and the CNTs were not removed significantly at 0.4-0.8m/s airflow. This is because the exfoliation effect of airflow on CNTs cannot completely overcome the Van der Waals force of \( \sigma_3 \), resulting in the presence of a large amount of \( \sigma_3 \). When the flow velocity increased to 1.2m/s, the content of CNTs in samples of all processing time decreased significantly, indicating that the peel force of CNTs at 1.2m/s had almost overcome the adhesion of \( \sigma_3 \). Therefore, a large number of CNTs were carried away by strong airflow. As the flow increased further, the loss of CNTs content decreased significantly and showed a stable trend (for example, the two points on the lower right corner were almost overlapped), further indicating that CNTs of \( \sigma_3 \) were almost completely peeled at 1.2m/s airflow. Meanwhile, SEM images of representative samples in Fig. 7 can also illustrate the same problem.
In Fig. 8, the relationship between coverage ratio of $\sigma_1$, $\sigma_2$ and $\sigma_3$ and processing time is calculated by the equation. It can be seen that there are $\sigma_1$, $\sigma_2$ and $\sigma_3$ in S1 and S2. Most of them are $\sigma_1$, but a small amount of $\sigma_2$ and a very small amount of $\sigma_3$. This is because CF in S1 and S2 have enough space for free adhesion of CNTs with various morphologies in the early stage of formation. Due to sufficient sizing agent, CNTs can be well absorbed and embedded, so there is more $\sigma_1$. In S3-S5, $\sigma_3$ started to increase and $\sigma_1/\sigma_2$ remained unchanged. This indicates that the surface space of CF is basically occupied by CNTs, and the subsequent CNTs can only be stacked on $\sigma_1$ and $\sigma_2$. Therefore, all the newly added CNTs are noted as $\sigma_3$.

### 3.3. Mechanical properties of composites and reinforcing mechanism

IFSS of S1-S5 and S1e-S5e are shown in Fig. 9. Without being purged, the change of IFSS was attributed to the common mechanical action of $\sigma_1$, $\sigma_2$ and $\sigma_3$, which was effective in improving the interface as a whole. When $t = 0.6s$, IFSS reached the maximum value of 35MPa, which was about 33.9% higher than that of the sample without modification. However, the longer processing time decreased IFSS, which was consistent with the surge of $\sigma_3$. From the perspective of the loose structure of $\sigma_3$, it is estimated preliminarily that the infiltration hindered by $\sigma_3$ between interface and resin or the interface defects caused by bubbles at the interface lead to it. However, after being purged at 2m/s, $\sigma_3$ were completely blown away from the CF surface. And only $\sigma_1$ and $\sigma_2$ had an effect on IFSS, and IFSS is stable between 32–35 MPa.

In order to precisely analyze the contributions of $\sigma_1$, $\sigma_2$ and $\sigma_3$ to interfacial mechanical properties respectively, the sample size was expanded by refining processing time. By turning $\sigma_2$ to $\sigma_1$, samples containing $\sigma_1$ only can be made. Figure 10(a) can be obtained through IFSS test. After the purging of $\sigma_3$, the samples contained only $\sigma_1$ and $\sigma_2$. And $\sigma_2$’s IFSS (Fig. 10(b)) is obtained by the IFSS of these sample subtracted those with same $\sigma_1$ content. Similarly, $\sigma_3$’s IFSS (Fig. 10(c)) is obtained by IFSS of unpurged samples subtracted those being purged.

As shown in Fig. 10, with the amount of CNTs increasing in $\sigma_1$, IFSS rapidly increased to 4MPa, and promptly decreased to 0 when the surface coverage was 20%, then negative effect was generated. The positive effect of $\sigma_1$ to IFSS was because the surface of CF becomes rougher [36]. However, in SEM images of Fig. 6, mechanical properties of a thin layer of high concentration CNTs in excessively thick $\sigma_1$ were weak. The interior of $\sigma_1$ broke first when the external force was applied, so that a great number of CNTs were exposed. Different from $\sigma_1$’s enhancement mechanism, $\sigma_2$ has distinct cross-interface features, which belong to anchoring effect [37]. This structure makes positive contributions to IFSS all the time and plays an even prominent role at a low content. At high concentration, its IFSS contribution tends to saturate to 6.5MPa. Compared Fig. 10(a) with (b), the interface enhancement of $\sigma_2$ was significantly stronger than that of $\sigma_1$ under the same CNTs concentration, indicating that the anchoring effect in interface enhancement was much better than the improvement of surface roughness. While $\sigma_3$ posed a completely negative effect on the interface, this may because its loose structure impeded the formation
and fusion of the interface, and that the surface tension of the resin compresses the interface layer to form a high concentration of CNTs isolated layer, resulting in a large number of defects existing in the interface layer.

4. Conclusions

(1) The surface of CF containing sizing agent could form three types of CNTs in the way of using plasma gas-phase dispersion and spraying. They are complete embedding type (σ₁), partial embedding type (σ₂) and sufficient exposure type (σ₃). σ₁ and σ₂ generate synchronously. At the beginning of spraying, σ₁ and σ₂ are mainly formed and σ₁/σ₂ gradually decreased. In the later period of spraying, the content of σ₁ and σ₂ no longer increases and all the newly added CNTs are σ₃.

(2) The low content (20%) of σ₁ has a positive effect on IFSS, contributing 4MPa maximally. And the high content (20%) of σ₁ has a negative effect on IFSS. σ₂ plays a positive role on IFSS all the time, contributing 6.5MPa maximally. σ₂ is significantly better than σ₁ at the same concentration. σ₃ has a negative effect on IFSS all along.

(3) As a whole, IFSS of CF processed by CNTs could reach 32-35 MPa, increasing 33.9% maximally. σ₁ and σ₂ is the main reason for the improvement.

Declarations

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Credit authorship contribution statement


Acknowledgements

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Data availability
The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

Financial information statement

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References


Figures
Figure 1
(a) The form of CNTs in liquid phase on the surface of CF [24]. (b) the form of CVD modified CNTs on the surface of CF [25]. (c) the form of excess CNTs in vapor deposition on the surface of CF.

Figure 2
(a) The process of dispersing CNTs into gas phase and of spraying.
(b) the process of purging.
Figure 3

Diagram of turning $\sigma_2$ to $\sigma_1$. It can be seen that liquid surface tension posed a significant influence on the distribution of CNTs, which is making most CNTs stick close to the surface of CF without changing the quantity of CNTs on the surface of CF.
Figure 4
SEM image processing procedure and signal recognition type.

Figure 5
SEM image of CNTs on the surface of CF at different deposition time. (a) without being purged (b) purge at 2.0 m/s.

Figure 6

The fracture surface of resin balls being tensile and peeling.

Figure 7

Coverage of CNTs on the surface of CF under different purging conditions.
Figure 8

Relations between the coverage ratio of $\sigma_1$, $\sigma_2$ and $\sigma_3$ and processing time.
Figure 9

Different IFSS of CF under different deposition time.

Figure 10

The contribution of coverage ratio of three types to IFSS.