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Interfacial and fatigue-resistant synergetic enhancement of carbon fiber/epoxy hierarchical composites via an electrophoresis deposited carbon nanotube-toughened transition layer

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ABSTRACT

To synergistically improve interfacial and fatigue-resistant performance of carbon fiber/epoxy composites, a transition layer reinforced by oxidized multiwall carbon nanotubes (OCNTs) was built. OCNTs were integrated onto carbon fibers using a continuous electrophoretic deposition method. Results of static and fatigue tests showed that compared with composites without OCNTs, the hierarchical composites not only showed increases of 33.3% in interfacial shear strength, 10.5% in interlaminar shear strength and 9.5% in flexural strength but also acquired 4.5% improvement in residual bending strength retention after fatigue tests. The transition layer detected by energy dispersive X-ray spectroscopy and atomic force microscope in force mode might be responsible for the above improvements. Combined with scanning electron microscopy analysis and ultrasonic C-scan detection, the functions of modified interfacial microstructure were discussed. The enhanced interface could help to reduce stress concentration and lead destructive cracks to spread along multiple paths, enhancing the damage resistance.

1. Introduction

The mechanical properties and versatilities of carbon fiber reinforced polymer matrix composites have made them favorable for many engineering applications [1,2]. However, due to the poor infiltration of resin and the performance mismatch between carbon fiber (CF) and resin matrix, interfacial debonding and earlier damage tend to occur under external loading [3,4]. In addition, the composites are sensitive to damages caused by repeated fatigue loads, and the anti-fatigue property of these materials directly affects the safety, reliability and economic applicability of the composite parts [5]. Therefore, both the ideal interfacial binding and fatigue resistance properties are inevitable requirements for composites.

The microstructure of interface not only has decisive influence on the performance of composites, but also is important for fatigue behavior which directly control the crack direction and the damage development [6]. In general, when the improvement of the fiber/-matrix adhesion is achieved, the fatigue performance of composites could be enhanced if keeping the other parameters (like loading) constant due to the improved load transfer efficiency of interface [7]. However, a high fiber/matrix interfacial bond tends to cause the brittle behavior of matrix and stress concentrations around the fiber which is unfavorable to the absorption and release of fatigue energy [8,9]. In order to achieve the expected mechanical properties of carbon fiber composites, more studies are needed to well understand the coupling relationship between interfacial and anti-fatigue properties in fiber composites.

Does the trade-off between the interfacial and anti-fatigue performance be achieved by optimization of the interface microstructure? Recently, many efforts have been focused on improving the properties of fiber-reinforced polymer composites, among which the progress made in hierarchical composites with carbon nanomaterials (like nanotubes and graphene) as auxiliary reinforcement is very attractive [10,11]. Our group has found that the graphene or carbon nanotubes (CNTs) based interface layer could enhance the load transfer from matrix to fillers and reduce interfacial stress concentrations [12–14]. As for the anti-fatigue performance of fiber composites, studies in literature have found that the incorporation of nanoparticles into the polymer matrix would result in an improved anti-fatigue performance, which is considered to be caused by the retardation of matrix crack formation

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and decrease of the density of transverse cracks [15–19]. But transverse cracks formed by linkage of individual matrix crack occurred at interface or matrix highly depends on the fiber/matrix interface [7]. And the interfacial stress concentration, which is one of the main mechanisms to control the fatigue life of composites, also affects the fatigue property of composites greatly [20,21]. Therefore, the excellent interface region with intermediate modulus serving as a stress transfer medium may achieve the synergistic enhancement of interfacial and anti-fatigue properties. However, up to now, few researches were systematically conducted on improving the interfacial and anti-fatigue performance of carbon fiber/epoxy composites by modifying interfacial microstructure. And there are few reports about the coupling relationship between interfacial and anti-fatigue performance and specific damage mechanisms of CF composites on the nano- or micro-scale arising from carbon nanomaterials.

With large specific surface area, excellent mechanical properties, as well as good compatibility with polymer [22], CNTs have been considered to be applied as the modifiers of traditional composites in order to enhance the mechanical, thermal and electric properties [23–25]. So far, the methods used to incorporate CNTs onto carbon fiber surface can be divided into two categories: chemically grafted and physically absorbed. Both chemical vapor deposition [26,27] and chemical grafting [28,29] could directly "grow" CNTs on the fiber surface with strong grafting force, which took advantage of the "bridge" function of CNTs between fiber and resin [30]. Other methods which lay emphasis on the CNTs enhancement of surrounding resin near fibers [12] by depositing CNTs onto fiber surface including dip coating [31–33], sizing [34] and electrophoretic deposition (EPD) [35–37] processes were based on physical interactions. EPD is an effective and versatile approach for the deposition of CNTs on the CF surface, which can be readily automated and utilized for industrial applications. In this work, we plan to use EPD method to build an interface transition layer by toughing the interface using CNTs.

In this paper, we conducted a study to synergistically enhance the interfacial and anti-fatigue performance of CF/epoxy hierarchal composites with CNTs reinforced transition layer. Therefore, a feasibility of EPD manufacturing process was used to facilitate a dispersion of CNTs in the small inter-fiber-spaces of CFs. The fabricated CNTs-CFs were successfully infiltrated with epoxy resin using resin transfer moulding technology. In mechanical experiments the specimens were exposed to static and cyclic loading to investigate the influence of the modified interfacial microstructure on the interfacial property and fatigue degradation. Residual strength, which is often based on the fatigue life prediction of composite materials, was obtained to elucidate damage capacity of composites. Interface microstructure detection was conducted by energy dispersive X-ray spectroscopy (EDS) and atomic force microscope (AFM) to verify the existence of transition interphase. Finally, the anti-fatigue enhancement mechanisms were discussed in detail by the combination analysis of fractographic scanning electron microscope (SEM) and ultrasonic C-scan.

2. Experiment section

2.1. Materials

Multi-wall carbon nanotubes (diameters of 30–50 nm and length of 10–20 μm) were purchased from Shenzhen Nanotech. Port. Co. Ltd., China, which had been proved to be good for dispersion and deposition effect for EPD [12]. T700S carbon fibers (12 K, 1.78 g cm^{-3}), obtained from Japan Toray, were used as reinforcing filler. JC-02A modified epoxy (epoxy value 0.51–0.53) and JH-0511 modified 2-ethyl-4-methylimidazole, used as accelerant, were obtained from Changshu Jia Fa Chemical Co. Ltd., China. The curing agent, tetrahydrophthalic anhydride was supplied by Wenzhou Qingming Chemical, China. The sizing on CF had been removed in all samples to facilitate dispersion of OCNTs.

2.2. Preparation of oxidized carbon nanotubes (OCNTs)

In order to remove the impurities and introduce carboxyl groups on the surface of CNTs, 2 g of raw CNTs were immersed in 160 ml solution of HNO_3/H_2SO_4 (1/3, v/v) and heated to 70 °C for 8 h [38]. The mixture was diluted with pure water and filtered through a membrane with 0.45 mm pore size. The oxidized carbon nanotubes (OCNTs) were washed repeatedly with pure water to reach a neutral pH and dried at 55 °C in vacuum for 24 h.

2.3. Electrophoretic deposition of OCNTs onto CF surface

First, CF desizing was carried out by refluxing in acetone at 80 °C for 24 h. This pretreatment was to exclude sizing clustering effect on CFs, so as to facilitate a dispersion of OCNTs in the small inter-fiber-spaces of CF bundles. The OCNTs were dispersed in deionized water by ultrasonication for 2 h at a loading of 0.3 mg/ml which was conducive to form a stable suspension for the good deposition effect on fiber during EPD process [39]. Afterwards, the tank filled with OCNTs suspension was put in an ultrasonic bath. The CF tow, as the deposition electrode, was placed in the middle of the two metallic electrodes which were used as counter electrodes with 9 cm distance. Ultrasonication was applied before each EPD process to widen the space between CFs as well as to remove the tiny bubbles caused by water electrolysis, which could help to obtain a distribution of OCNTs on single CF. During EPD, the negatively charged OCNTs would migrate towards the CF electrode when a direct current voltage of 24 V was applied which was a relatively small voltage [40–42]. The amount of OCNTs deposited onto CF was controlled by deposition time. In this experiment, the deposition time was ranged from 1 to 7 min, by which CF-based reinforcements doped with different contents of OCNTs were prepared and the samples were denoted as OCNTs-CF1, OCNTs-CF3, OCNTs-CF5, OCNTs-CF7, respectively. After the EPD process, the CF tows were baked out using a heating oven, and then wound up on a roller. The EPD procedure for preparation of CNTs-coated CF is illustrated in Fig. 1. Similar methods could also be found in previous literatures [43–45].

2.4. Preparation of unidirectional composite samples

The unidirectional CF reinforced composites were produced via the resin transfer moulding process. First, various CF tows were laid up straight in the 220 × 10 × 2.5 mm grooves in mould and the fiber volume fraction of composite was kept at about 45%. The epoxy resin, harder and accelerant were mixed at the weight ratio of 100:70:1, and then pressed into the mould under the pressure of 0.1 MPa. The mixture was cured in a heating oven according to a curing step at 90 °C for 3 h, 120 °C for 3 h and 150 °C for 5 h.

2.5. Preparation of single fiber-composite samples

The procedures of preparation of the single fiber-composite fragmentation samples are as follows. Single carbon fiber was carefully separated from the fiber tows. Then, the single fiber was positioned in the center of a mould with a dogbone shaped cavity. The two ends of fiber extended over the mould and were stuck to a piece of plastic with certain weight to make the fiber straight in the sample. Subsequently, the epoxy resin system was cast into the mould, embedding the fiber completely. The curing temperature and procedure were as described above.

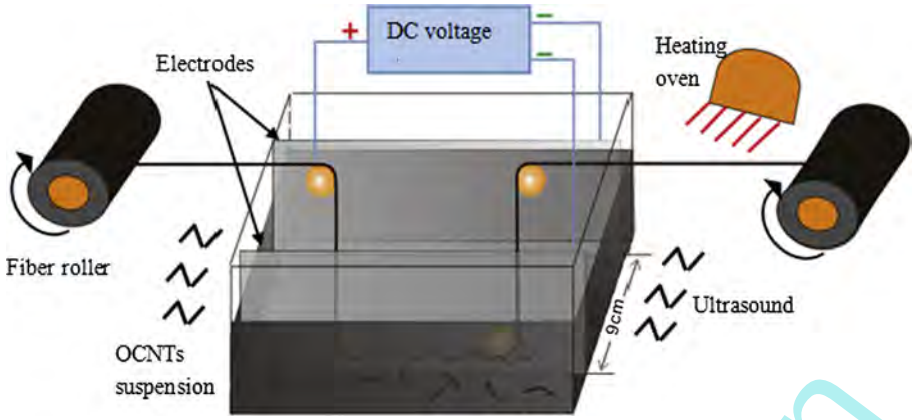

Fig. 1. Schematic of the EPD procedure [43–45]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.6. Characterization techniques

Transmission electron microscopy (TEM) observation of CNTs was performed using a Hitachi 7650 operated at 200 kV. The chemical composition of CNTs was analyzed by Fourier transform infrared spectroscopy (FTIR, Bruker Tensor 37) and X-ray photoelectron spectroscopy (XPS, PHI 5700) with Al Ka excitation radiation.

The short beam shear tests and flexural tests were carried out according to JC/T773-2010 and ASTM D790-03 standards, respectively. The short beam specimens (20 × 10 × 2.5 mm) and flexural specimens (50 × 10 × 2.5 mm) were cut from the composites. Both tests were performed in a universal testing machine (Instron 3369, USA) and the final values were calculated as averages of five specimens for each composite. To assess the influence of CNTs on the interfacial bonding, the interfacial shear strength (IFSS) of OCNT-deposited CFs in epoxy was tested by means of single fiber-composite fragmentation, and IFSS, τ, can be estimated from Kelly-Tyson model [46,47]:

$$\tau = \frac{\sigma_f d}{2L_c}$$

$$L_c = \frac{4L}{3}$$

$$\sigma_f = \sigma_0 \left(\frac{L_0}{L_c}\right)^{\frac{1}{\beta}}$$

where d is the fiber diameter, σ_f is the fiber strength at the critical fragment length, Lc, which can be obtained from the mean fiber fragment length, L, at crack saturation. L_0 is initial length of the single carbon fiber (25 mm in this study), σ_0 is the fiber tensile stress at the point of first fiber fragment, and β is Weibull shape parameter determined from the curve of fiber tensile stress vs. fragment length. It can be seen from the above formulas that comparing two fibers of equal strength, strength distribution and diameter, the fiber with the shortest critical length will have the highest IFSS.

The bending fatigue was carried out on electronic universal testing machine (Instron E10000, USA). The baseline composites and the composites with the highest interfacial performance were subjected to tests. The cyclic fatigue tests were conducted in a loading frequency of 10 Hz, and a stress ratio of 0.1. The baseline composites specimens were identified with a total lifetime of approximately 60,000 cycles at the level of applied loads σ_{max} = 729 MPa (80% flexural strength). The main goal was to evaluate the fatigue endurance prosperities of both composites. After approximately 30,000 cycles (50% lifetime), the specimens were took off for static tests to obtain residual bending strength values.

Morphologies of CFs and fracture surface of composite specimens were observed using field-emission scanning electron microscope (SEM, Hitachi S-4800) at an accelerating voltage of 10 kV. All the samples for SEM were coated with a layer of gold before test to improve conductivity. The internal damage of the composite samples was evaluated by using water immersion focusing method in an ultrasonic C-scan inspection system (BSN-C3409, China). The scanning mode is fixed depth mode and the frequency is 5 MHz. The interfacial microstructures of composites were studied by energy dispersive X-ray spectroscopy (EDS, JEOL JSM-5900LV, Japan) equipped on SEM and force modulation atomic force microscope (AFM, CSPM 5500, China) to evaluate the carbon element and relative modulus distribution in the interface layer of composites, respectively. The cross-sections of composite specimens were polished to ensure the testing accuracy.

3. Results and discussion

3.1. Morphology, composition and dispersion of CNTs and OCNTs

TEM were utilized to characterize the surface morphology of OCNTs. The raw CNTs were shortened to the length of 0.2–1.0 μm with a strong acid mixture treatment (see Supporting Information, Fig. S1). As shown in Fig. 2, the appearance of a band at 1706 cm^{-1} could be assigned to the stretching vibrations of carbonyl groups (C═O), arising from the ─COOH moieties introduced to the sidewalls and open ends of CNTs after the oxidative treatment [29,48]. XPS analysis was also employed to elucidate the chemical composition of CNTs and OCNTs. The oxygen element concentration and O/C atomic ratio of OCNTs increased by 692% and 786%, respectively, compared with that of raw CNTs (see Supporting Information, Table S1). The shortened length and the increase of hydrophilic functional groups both contributed to the good dispersibility of OCNTs in pure water.

3.2. Surface characteristics of CNTs–CF hybrids

Characterization of the CF surfaces before and after EPD of OCNTs was performed by SEM imaging. As could be seen in Fig. 3, after refluxing in acetone, the polymer attached on the CF surface disappeared (Fig. 3a), and a few shallow narrow parallel grooves were observed along the fiber axis (Fig. 3b). Fig. 3c–f showed the surface topographies of CF surfaces treated with OCNTs. As shown in Fig. S2, the thickness of the films formed with randomly orientated OCNTs was in a wide range from tens of nanometers to several hundred nanometers by adjusting deposition time. From Fig. 3e and f, the coating thickness increased with

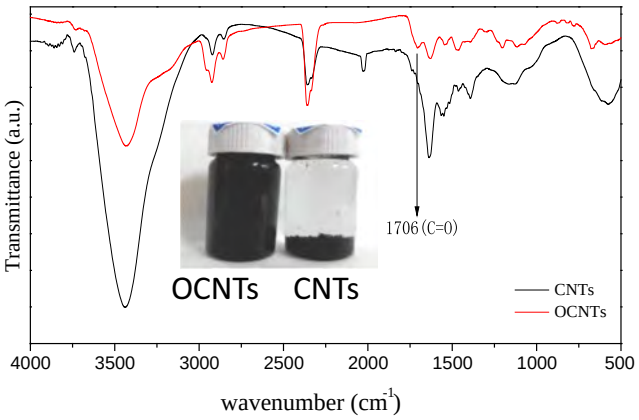

Fig. 2. FTIR of raw CNTs and OCNTs. The inset image showed the stability of CNTs in water, two weeks after the dispersions have been prepared. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the increasing deposition time. OCNTs-CF1 presented a partial OCNTs coverage of CF surface and as the deposition time prolonged, more CNTs were attached onto CFs. Especially for the OCNTs-CF5, it exhibited a full OCNTs surface coverage (Fig. 3e). However, on the surface of OCNTs-CF7, the agglomeration of some OCNTs (marked in circles) was observed. Meanwhile, we have measured the weight change of composites before and after EPD process (see Supporting Information, Table S2). This uniform deposition of OCNTs could increase the surface area of CFs and consequently impart a mechanical interlocking with the matrix [2,41]. However, as shown in Fig. 3f, some agglomerations of OCNTs (marked in circles) were observed on the surface of OCNTs-CF7, which might result in deterioration of interfacial properties [49].

3.3. Mechanical properties of composites

3.3.1. Interlaminar shear properties

The interlaminar shear strength (ILSS) was used to quantify the interfacial properties between the CFs and the resin matrix [50]. From the data in Fig. 4a, a conclusion can be drawn that the ILSS may be highly dependent on the quantity and distribution state of OCNTs in the interfacial region [36]. In detail, the ILSS of OCNTs modified composites is obviously higher than that of the baseline composites, especially OCNTs-CF5/epoxy yielding ILSS of 88.25 MPa, which had an increase of 10.5% in comparison with CF/epoxy composites. These results demonstrated that the introduction of OCNTs surrounding the fiber in composites contributed to the improvement in interfacial property. Moreover, the hydroxyl and carboxyl functional groups of OCNTs, interacting covalently with the epoxy chains [32], could also promote interfacial adhesion. However, as expected, the ILSS of OCNTs-CF7/epoxy decreased compared with that of OCNTs-CF5/epoxy. The results might be due to the fact that agglomerations of OCNTs were anticipated to act as imperfections in interfacial regions, which overroded stress transferring effects of the interface and resulted in deterioration of interfacial strength [51,52].

3.3.2. Flexural properties

As shown in Fig. 4b and c, the static three-point bending test of unidirectional CF composites was conducted to obtain the ultimate bending strength, bending modulus, load-deflection curves. It was clearly demonstrated that the OCNTs deposition endowed the hierarchical composites with a higher flexural strength and modulus than the baseline composites. The elongation of OCNTs deposition time led to a gradual increase in the flexural strength and the OCNTs-CF5/epoxy composites showed a maximum strength (997.70 MPa) and modulus value (69.64 GPa), with an improvement of 9.46% and 15.4% compared with baseline composites, respectively. Conversely, a further extension of EPD time led to a decline in bending properties. The degradation in the mechanical properties could be associated with the deterioration of OCNTs dispersibility in interface region.

3.3.3. Interfacial shear properties

To further confirm the role of OCNTs introduction in interface phase, the baseline composites and composites with 5-min deposition of OCNTs were tested by single fiber fragmentation test, and the results were given in Table 1. Predictably, the deposition of OCNTs gave rise to a significant increase of the IFSS (about 33%). The critical fragment length showed that the composite specimen with the OCNTs displayed shorter fragment length than that without OCNTs (Fig. 5). These results were consistent with the measured IFSS, demonstrating that the OCNT-deposition process improved fiber/matrix interfacial adhesion and CF was difficult to be drawn out under external force.

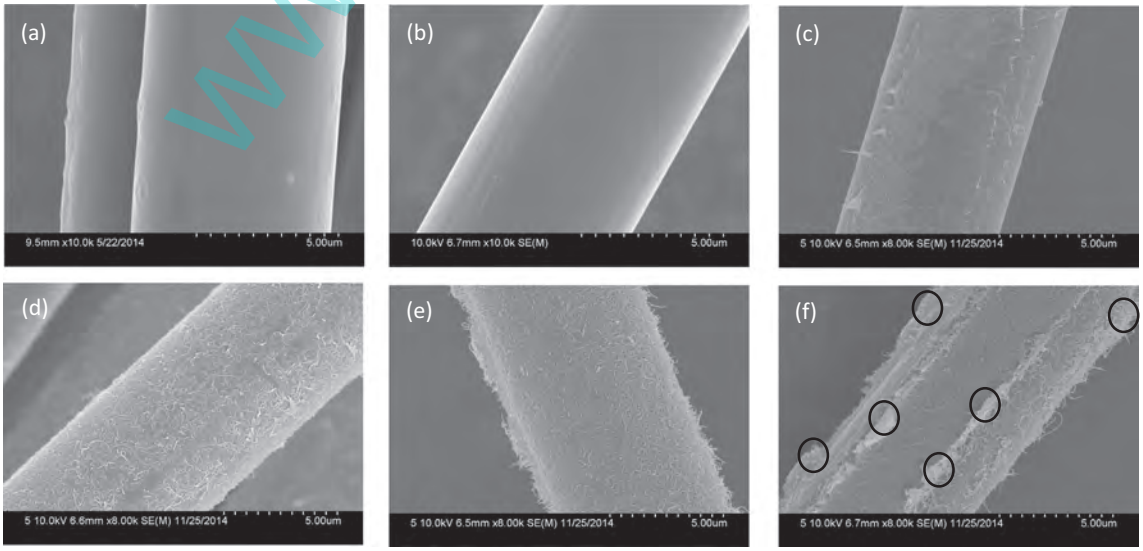

Fig. 3. SEM images of (a) as-received CF, (b) desized CF, (c) OCNTs-CF1, (d) OCNTs-CF3, (e) OCNTs-CF5, (f) OCNTs-CF7.

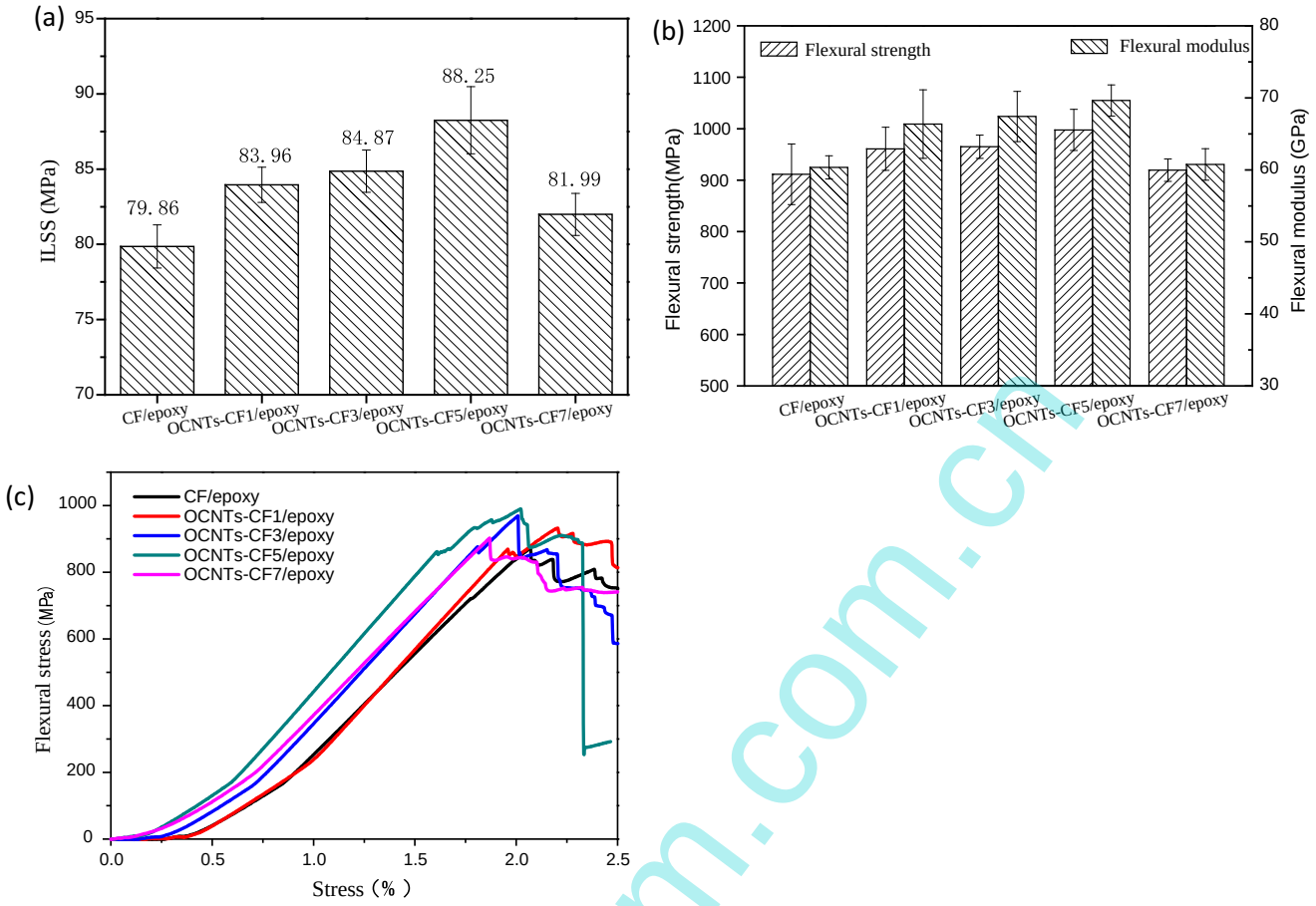

Fig. 4. Interlaminar shear strength (ILSS) of composites. (a) Flexural properties of composites. (b) Flexural strength and modulus. (c) Flexural stress-strain curves. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Fragmentation test results.

Fiber types	Fiber tensile strength (σ_0 (MPa))	Weibull shape parameter (β)	IFSS (τ (MPa))
CF	4833 ± 403	4.51 ± 0.24	54 ± 5
OCNTs-CF5	4896 ± 568	4.53 ± 0.70	72 ± 7

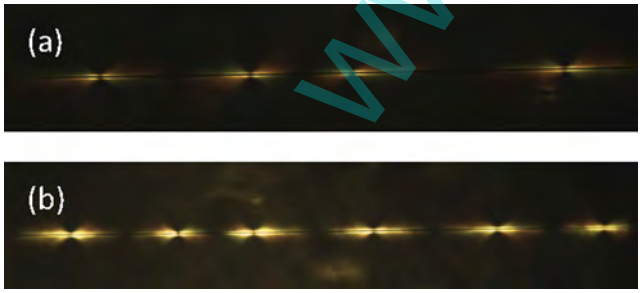

Fig. 5. Birefringence effects of fragmented specimens. (a) Desized CF (b) OCNTs-CF5. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.3.4. Fatigue-resistant properties

To verify whether the interfacial and anti-fatigue performance can be improved simultaneously, the composites of OCNTs-CF5 and the baseline composites were subjected to bending fatigue tests. The residual strength of composite materials under fatigue loading is one of the important properties of composites, which is often based on the fatigue life prediction of composites [53]. With an increase in the number of loading cycles, the accumulation of damage leads to a change in the macroscopic mechanical properties of the composites, such as the degradation of strength of materials [54]. To determine the bending stress degradation behavior, we took off composite specimens after approximately 30,000 cycles (50% baseline composite lifetime under 80% flexural strength) bending behavior (operated at a fatigue testing machine, E10000, shown in supporting information Fig. S2) and tested the residual bending strength on the static universal testing machine under the same condition as Section 3.3.2. As revealed in Fig. 6, the residual bending strength retention of OCNTs-CF5/epoxy specimens was 4.5% higher than that of baseline specimens, which meant the increase of composite fatigue resistance performance could be mainly attributed to the presence of OCNTs in interphase. When the composites were under loading, the cracks in the matrix propagated to the fibers. The direction of crack propagation was decided by the stress field of crack tip and the mechanical properties of interphase and fibers. As shown in Fig. 7b, the OCNTs interphase working as a shielding layer which could relieve the stress concentration, prevented the crack tips to directly contact with the fiber surface and made the crack path deviate away from the fiber surface to the interphase region [55]. Moreover, numerous OCNTs on the fiber surface could induce more cracks when the major crack passed to them (Fig. 7), which could efficiently absorb the fracture energy [6]. Therefore, EPD offers interfacial and fatigue-resistant synergetic enhancement of carbon fiber/epoxy

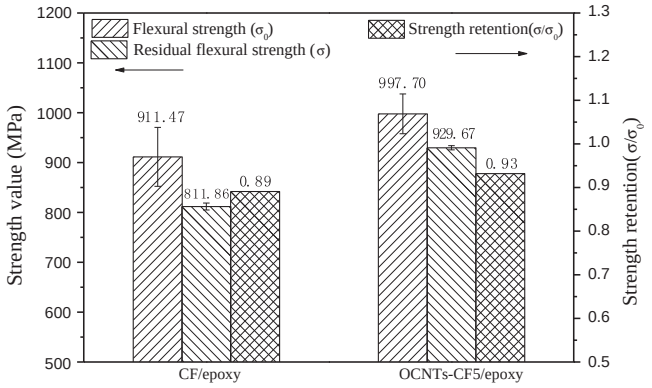

Fig. 6. Flexural strength and residual flexural strength retention of CF/epoxy and OCNTs-CF5/epoxy composites.

hierarchical composites via ONCTs-toughened transition layer compared with other techniques (Table S3).

3.4. Microstructure of interphase

In the composite moulding process, with resin infiltrating, some OCNTs may drop from fiber surface and diffuse into matrix and a transition interface layer (Fig. S2) which has a certain thickness might be formed (Fig. 8). As shown in Fig. 7a, the stress concentration of composites without OCNTs is produced in the major cracks and the direction of crack propagation. For OCNTs-CF/epoxy composites (Fig. 7b), it may eventually be beneficial to decrease stress concentration and raise the mechanical properties of composites due to the presence of OCNTs. To conclusively demonstrate this hypothesis, we detected the interfacial microstructure adopting two methods to illustrate OCNTs effect on interface region.

The distribution of carbon element across the cross-section of composites was manifested by EDS mapping and linear scanning spectra. For the CF/epoxy composites, the outline of CF was obvious and the amount of carbon element dropped suddenly along the white line (shown in Fig. 9a) from left to right (Fig. 9b), which illustrated the great difference of carbon content in CF and matrix. Whereas in the cross-section of OCNTs-CF5/epoxy composites, it was difficult to distinguish boundary between fiber and matrix (Fig. S4(b)), which meant an increasing of carbon element content, indicating the presence of CNTs in interphase. Therefore, a transition layer composed by OCNTs and epoxy was formed in hierarchal composites.

The force modulation AFM was used to characterize surface relative modulus distribution images of materials, which can provide the performance information of different components of composites. In previous reports, the effective interphase thickness values were accurately measured to research the interface properties by nanoscratch test [56]. Fig. 10 showed the f-AFM images and the corresponding cross-sectional analysis of the CF/epoxy and OCNTs-CF5/epoxy composites. From Fig. 10a, no striking interface region was observed between the CF and epoxy matrix region in composites and the modulus was observed to sharply change from the CFs to the epoxy matrix region (Fig. 10b). The CF reinforcement and epoxy matrix could be distinguished clearly from Fig. 10a. However, for OCNTs-CF5/epoxy composites, there was an obvious transition layer between CFs and matrix in Fig. 10c and d. The interphase was observed to have a moderate modulus, which was lower than that of the CFs and higher than that of the matrix, which is due to the existence of interphase composed of CNTs and epoxy matrix. This moderate interface can relieve the stress concentration effectively under static and dynamic loading conditions, and transfer the loads uniformly from the matrix to the CFs, and thus improve the damage resistance.

3.5. Interfacial and anti-fatigue reinforcing mechanisms

As aforementioned, significant improvements in interfacial and anti-fatigue performance for OCNT-deposited CF composites were observed compared with baseline composites. To elucidate the reinforcing mechanisms, fracture surface observation and internal damage detection were carried out.

3.5.1. Micrographs of static fracture surface

The SEM images in Fig. 11 depicted the fracture morphologies of the composites, showing a noticeable difference between the baseline and hybrid OCNTs-reinforced composites. The baseline composites with its neat epoxy matrix typically exhibited a smooth fracture surface (Fig. 11a). While in OCNTs-CF5/epoxy case (Fig. 11b), cohesive failure occurred since matrix and OCNTs were observed on the fibers after fracture process, indicating increased interfacial strength and the distribution state of OCNTs in the matrix surrounding CFs. Meanwhile, considerable plastic deformations of matrix can be seen on the fractographs, which meant that toughness increase of the interfacial region matrix. This improvement of the mechanical properties for the OCNTs-CF5/epoxy compared with that of CF/epoxy could be attributed to the local toughing of the polymeric matrix at the interphase region, which was favorable for releasing stress concentration and hindering the cracks propagate to CF surface. In addition, the nanoscale roughness, which increased fiber surface area, could further introduce a mechanical interlocking mechanism that was apparently effective in improving the interfacial strength between the fiber and matrix [57,58]. However, no crack bridging by CNTs is observed our study, and that may be related to the short length of OCNTs.

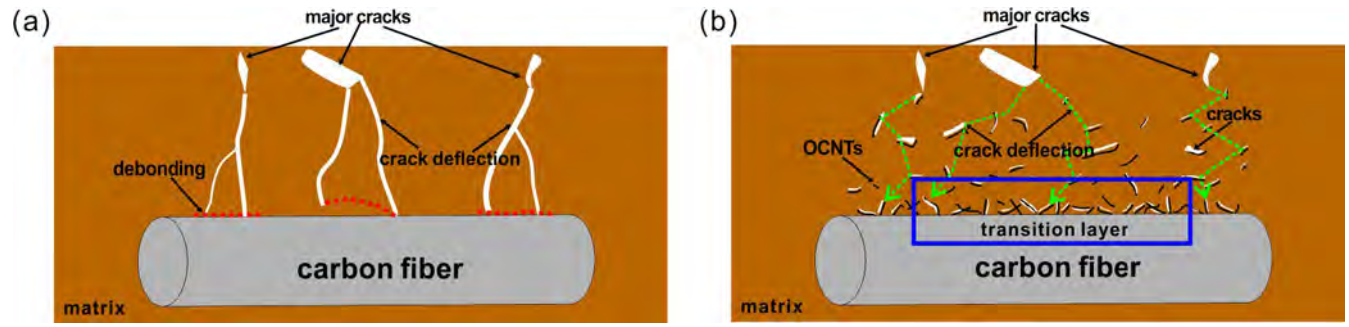

Fig. 7. Possible damage mechanisms of composites (a) without OCNTs and (b) with OCNTs. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

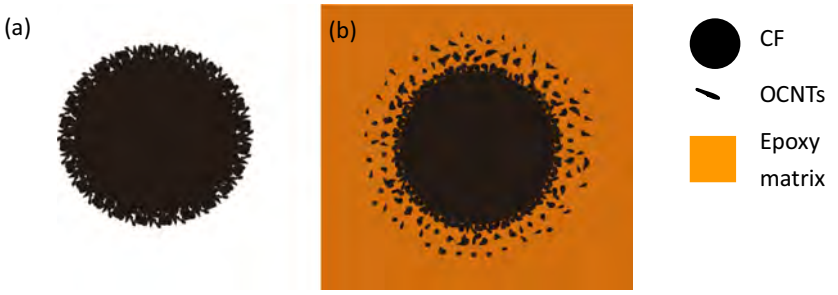

Fig. 8. (a) Illustration of the OCNTs-CF, (b) illustration of the formation transition layer. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

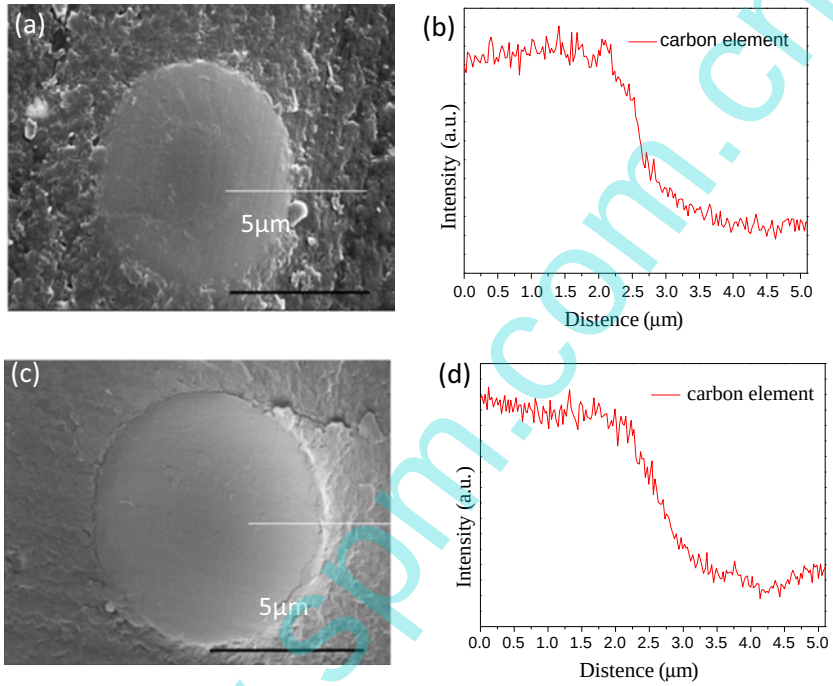

Fig. 9. (a) SEM image, and (b) linear distribution of carbon element content in CF/epoxy cross-section. (c) SEM image, and (d) linear distribution of carbon element content in OCNTs-CF5/epoxy composite cross-section. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.5.2. Internal damage detection with ultrasonic C-scans

To better understand the mechanisms responsible for the increase in fatigue resistance ability observed, we performed ultrasonic C-scan analysis of the composite samples prior to the residual bending strength tests. From Fig. 12a, the extent of damage for the OCNTs-CF5/epoxy composites was markedly lower than that of the baseline composites, which may be due to the fact that transition interface layer endow the hierarchical composite with bigger capacity for "damage accumulation". With the nanoparticle modification the damage mechanism level was shifted to the nano- and microscale level, which resulted in increased energy absorption and therefore a better ability to resist big deterioration damage.

3.5.3. Micrographs of composite fracture surfaces

Fig. 13 showed the fatigue fracture SEM images at different magnification of CF/epoxy and OCNTs-CF5/epoxy composites. At the bending cyclic loading mode, the composite top surface is under compression loading and the bottom surface is under tension loading. The damage fracture could be clearly divided into tension and compression side (Fig. 13a or d), and the damage modes consist of debonding between fiber and resin, fiber pull-out and fiber breakage. As shown in Fig. 13a and b, due to the lack of transition layer between CFs and matrix, the stress concentration on the CF surface cannot be released, which result in the severe fiber pull-out and delamination. Meanwhile, the major cracks appeared in baseline composite cross section (Fig. 13c) cause the stress concentration on the CF surface, resulting in fiber breakage and composite material failure. For OCNTs-CF5/epoxy composites, the OCNTs can relieve the stress concentration effectively under static and dynamic loading conditions, and transfer the loads uniformly from the matrix to the CFs, and more small cracks were aroused by adding OCNTs in interface (Fig. 13d–f).

We also examined the fracture surface after static bending tests to find out effects of the damage caused by cyclic fatigue on the crack propagation in the reloading process. For CF/epoxy (Fig. 14a–c), destructive cracks were derived from the fiber pull-out (Fig. 14b), and the direction of crack propagation was single due to the lack of energy release, and the cross section was seriously damaged due to the propagation of major cracks. Whereas in OCNTs-CF5/epoxy (Fig. 14d–f), the OCNTs in the matrix surrounding CFs can release stress concentration and hinder the cracks propagation to fiber surface, and the major cracks can spread along multiple paths. Finally, the interfacial and

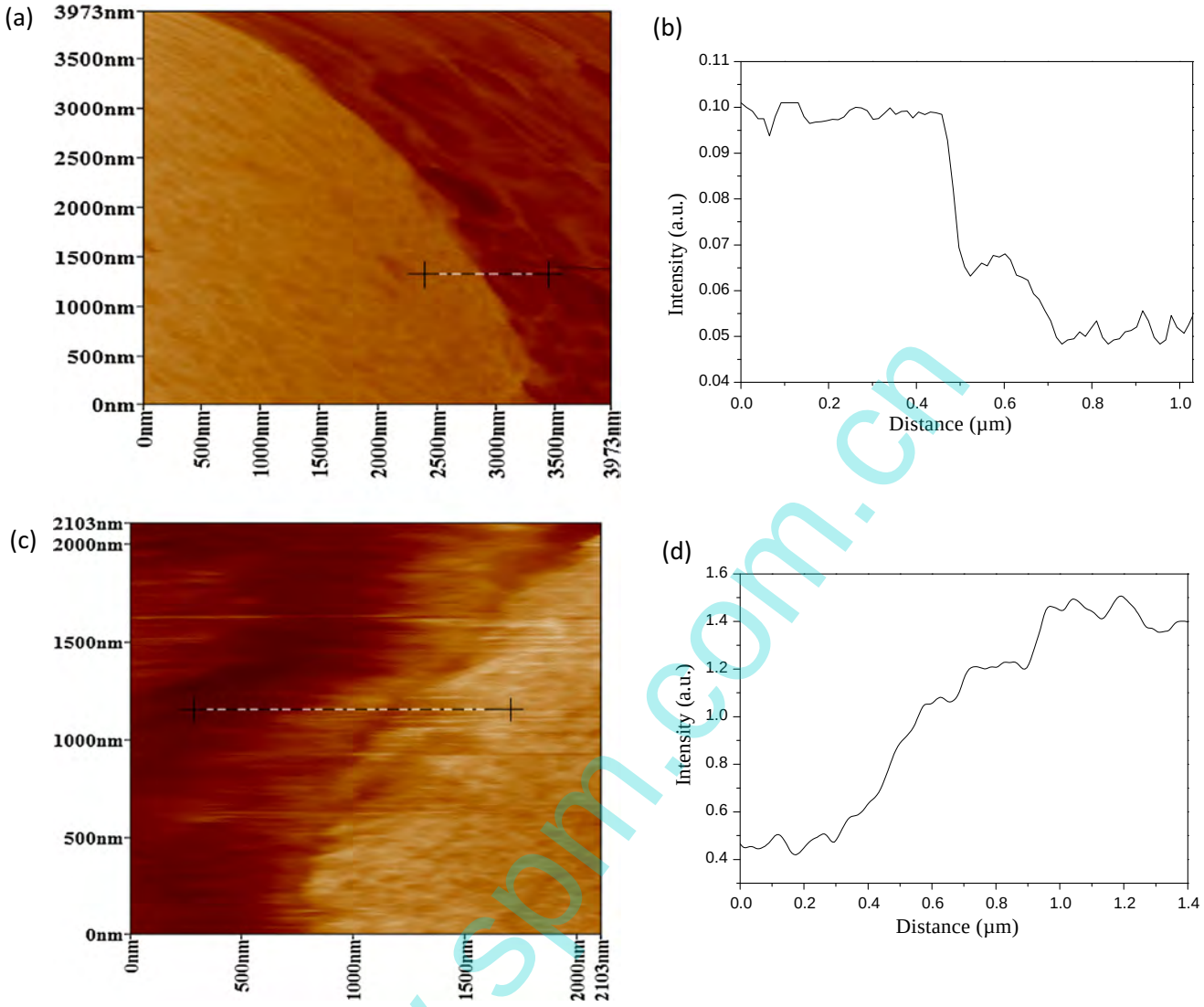

Fig. 10. CF/epoxy interphase: (a) relative modulus distribution image, (b) linear analysis of relative modulus; OCNTs-CF5/epoxy interphase: (c) relative modulus distribution image, (d) linear analysis of relative modulus. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

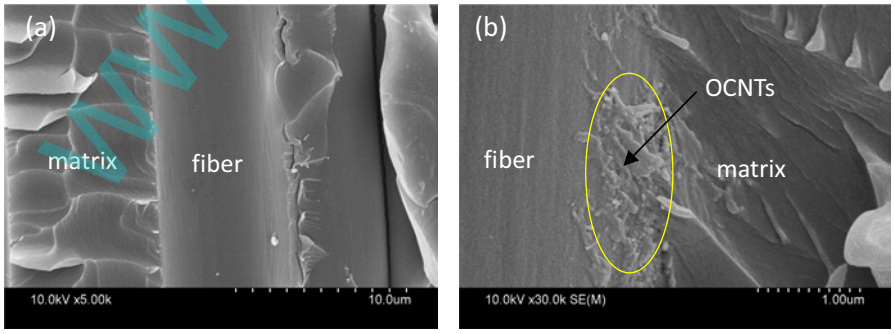

Fig. 11. SEM fracture surface morphologies of (a) CF/epoxy, (b) OCNTs-CF5/epoxy, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

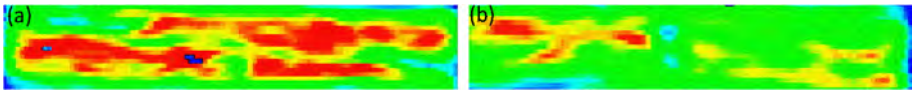

Fig. 12. Ultrasound analysis after 30,000 cycles of fatigue loading in bending mode at ~729 MPa (80% flexural strength) bending stress of (a) CF/epoxy and (b) OCNTs-CF5/epoxy samples. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

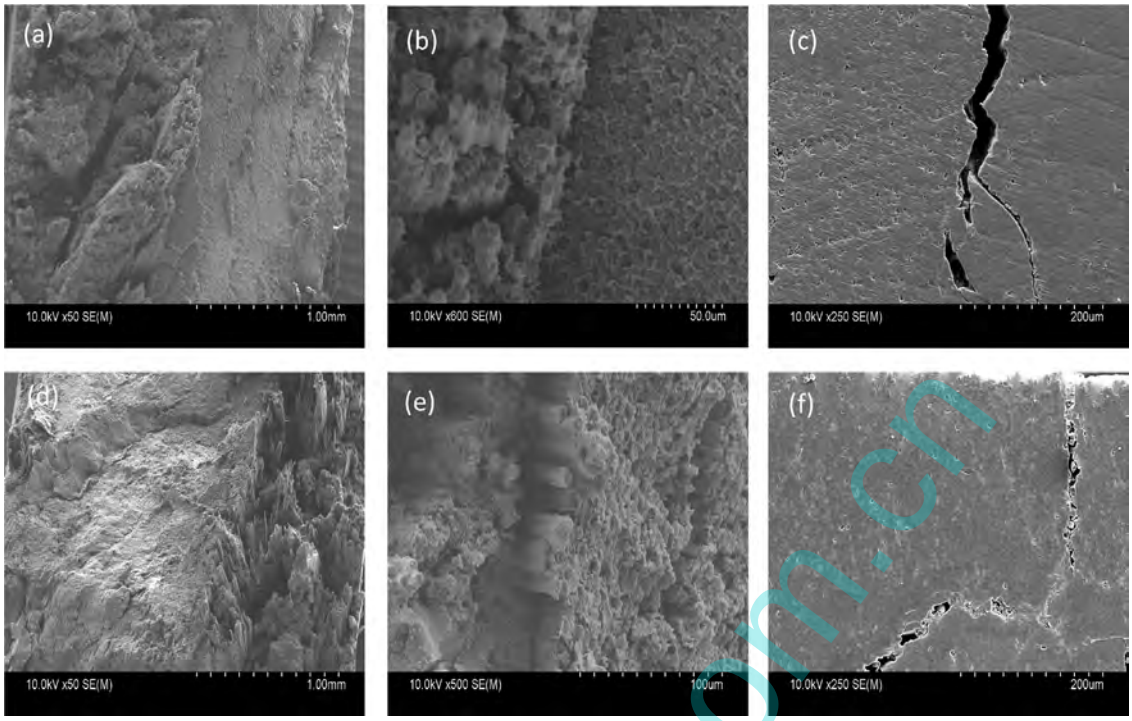

Fig. 13. SEM images of representative fracture surfaces from fatigue-fracture tests. CF/epoxy: (a) fracture morphology, (b) sectional view of image (a) with higher magnification, (c) fracture surface after polish. OCNTs-CF5/epoxy: (d) fracture morphology, (e) sectional view of image (d) with higher magnification, (f) fracture surface after polish.

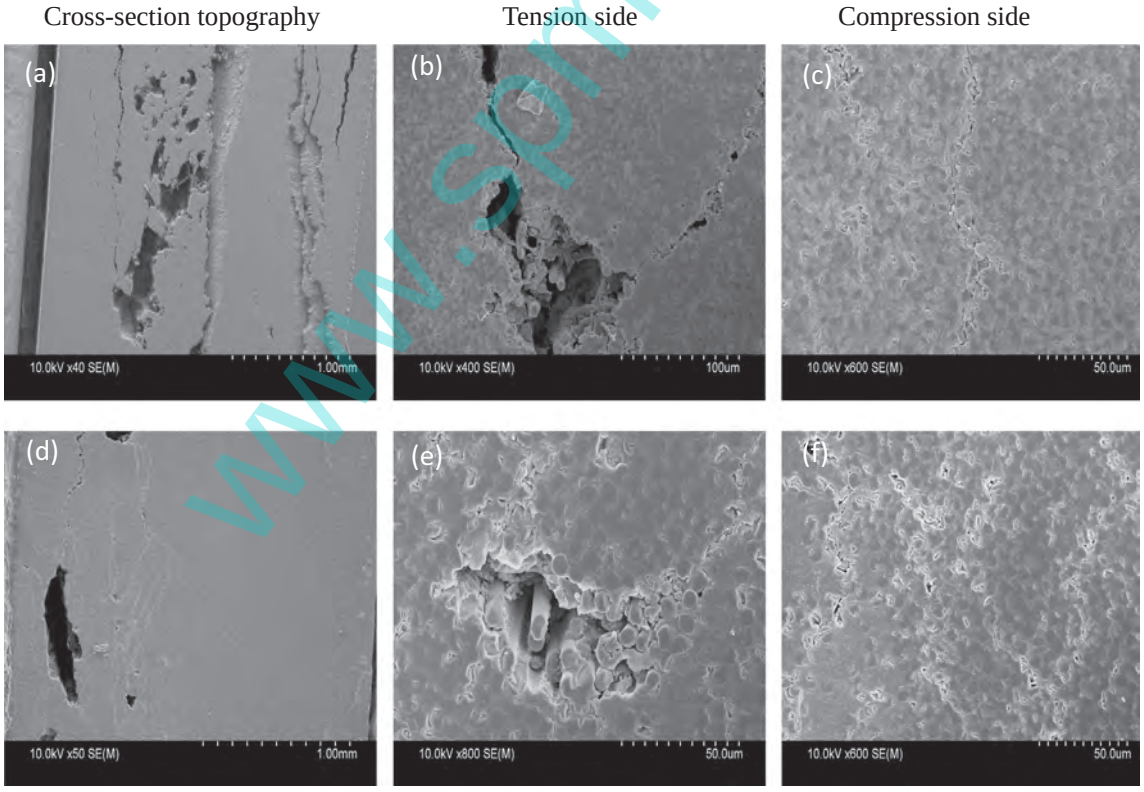

Fig. 14. SEM images of static bending fracture surface after repeated bending fatigue and polish. CF/epoxy: (a) fracture morphology, (b) tension side, (c) compression side. OCNTs-CF5/epoxy: (d) fracture morphology, (b) tension side, (c) compression side.

fatigue-resistant performance was enhanced by the transition layer reinforced by OCNTs.

Overall, the transition layer toughened by carbon nanotubes can significantly increase the load transfer ability of interface and

release stress concentration. The load, either static or dynamic, would be buffered and transferred from epoxy to reinforcing fillers uniformly. Therefore, the OCNTs/epoxy transition interphase would hinder the propagation of crack and improve the interfacial and anti-fatigue performance of carbon fiber reinforced polymer matrix composites.

4. Conclusions

Oxidized carbon nanotubes were deposited onto carbon fiber surface using a continuous EPD process to build a transition layer in fiber/matrix interface. This transition layer with intermediate modulus detected by SEM/EDS and the force modulation AFM is believed to be a key factor for the synergetic improvement of interfacial and anti-fatigue performance of CF/epoxy composites. As expected, results showed that 33.3%, 10.5%, 9.4% and 15.4% enhancements of hierarchal composites were observed in IFSS, ILSS, flexural strength and flexural modulus, respectively. When 5-min EPD treatment was conducted and the hierarchal composites also acquired 4.5% improvement in residual bending strength retention, showing a better damage resistance compared with the baseline composites. Based on the fracture morphology and internal damage, the interfacial and anti-fatigue reinforcing mechanisms were discussed. These results suggested that the enhanced load transfer ability of interface which could release stress concentration was responsible for the improvements in above mechanical performance. The OCNTs-toughed transition interphase could hinder crack from attacking directly fiber surface and generate enormous micro cracks to absorb destructive energy. The loads would be buffered and stress concentration would be relieved under static and dynamic loading conditions. Thus a rough sense was obtained about how the OCNTs reinforced transition layer would affect the interfacial and anti-fatigue properties of CF/epoxy composites.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.compositesa.2016.11.004.

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