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Optimization of interfacial microstructure and mechanical properties of carbon fiber/epoxy composites via carbon nanotube sizing

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ABSTRACT

Repetitious sizing treatment was used to modify the carbon fiber (CF) surface with carbon nanotubes (CNTs) for improving interfacial properties of CF/epoxy composites. Interlaminar shear and flexural results showed that mechanical properties of composites were significantly depended on the dispersion state and contents of CNTs in interfacial regions. Increases of 13.45% in interlaminar shear strength and 20.31% in flexural strength were achieved in quintuple sized-CF/epoxy composites, whereas excessive CNTs led to decrease of interfacial performance due to defects induced by agglomerated CNTs. Energy dispersive X-ray spectroscopy and force modulation atomic force microscope were used to detect the structure of interfacial phase and results indicated that gradient interfacial structure with various thicknesses was formed due to CNT incorporation. This means that such a simple and efficient method to improve interfacial performance of composites via regulating the fiber–matrix interphase structure was developed and showed great commercial application potential.

1. Introduction

Carbon fiber/epoxy composites, because of their favorable strength-to-weight and stiffness-to-weight ratios, are being used in many fields, such as aerospace, automotive, sports equipment and so on [1,2]. The interface, as a connection of fiber and matrix, affects the stress transfer efficiency, internal crack propagation, and the ultimate performance of composites [3–5]. However, the surface of carbon fibers is inertness and lack of reactive functional groups, which can result in weak cohesive force between carbon fibers and the matrix [6,7]. In addition, the huge gap between resin and carbon fiber in modulus and other physical properties will also affect the interfacial properties.

Carbon nanotubes (CNTs) have been widely used in enhancing composites for its large specific surface area, excellent mechanical properties, as well as good compatibility with polymer [8]. Introducing CNTs on the surface of fibers to improve the interfacial properties of composites has been a hot topic [9]. So far, several methods have been developed to introduce CNTs on fiber surface, such as chemical vapor deposition [10,11] and chemical grafting [12,13]. Both methods could effectively introduce CNTs on the surface of CFs with strong adhesion, but the use of high temperature and excessive chemical treatments has hindered their practical application. Electrophoretic deposition [14–16] is another efficient way to incorporate CNTs in composites. However, it was woven carbon fabric that was mostly used to receive CNTs, in which case CNTs were only deposited on part of the fiber surface rather than all surfaces [17]. Besides, the complicated process also limits its application in industrial scale. Compared to above methods, sizing or coating fibers with CNT-containing sizing agent [4,18–21] exhibit obvious advantages for their low-complexity and low-cost and show great potential application in industrial manufacturing of CNT/CF hybrid fibers.

Even though lots of work have been done in modifying composite interface, reinforcing mechanisms were mostly explained by combined effects of a variety of interface theories, like wetting [22], chemical bonding [12,19], mechanical interlock [22], local stiffening of the polymer matrix [23] and so on. And previous research tended to focus on how nanomaterials worked with fiber and matrix [10,24] rather than the relationships between interphase microstructure and properties of composites. According to previous research, CNTs can effectively suppress the formation and propagation of micro-cracks in the interphase due to the pullout of CNTs from matrix [25–27] or the bridging and anchorage between

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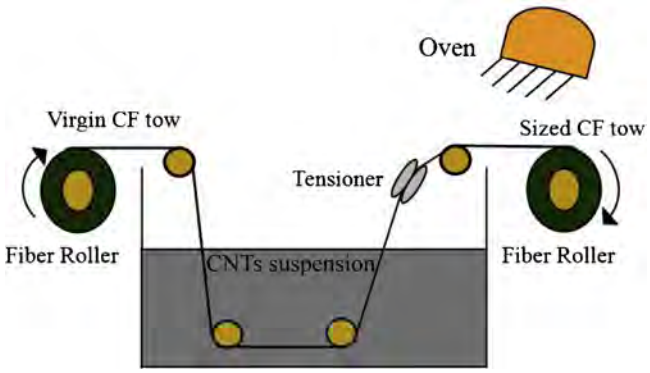

Fig. 1. Schematic of manufacturing sized carbon fiber.

CF and resin caused by CNTs [28]. However, the reality that the incorporated CNTs could "harden" the interface and an interphase structure different from CF and matrix might be formed has been neglected. Our previous research has confirmed that a gradient interphase structure between fiber and matrix was effective to transfer stress during loading [29,30], which is different from the reported mechanisms of improving interfacial properties.

The purpose of this paper is to explore the interfacial microstructure changes brought by incorporating CNTs using multi-sizing process, and then investigate the relationship between interface microstructure and composite performance. The sizing suspension with low concentration and good dispersion state was used to repeatedly modify the surface of CF, which is expected to result in a good distribution of CNTs on CF surface. The interface properties of composites were evaluated by three-point short beam shear tests and flexural tests. The distribution of CNTs on CF surface and fracture surfaces of composite specimens were detected by scanning electron microscopy (SEM). To investigate the reinforcing mechanism, the energy dispersive X-ray spectroscopy (EDS)/SEM and force modulation atomic force microscope (f-AFM) were used to analyze the structure of interfacial phase.

2. Experiment

2.1. Materials

The nanomaterials used in this study were as-received short hydroxyl multi-wall carbon nanotubes (95% purity, 0.5–2 μm in length, —OH content 1.76%) purchased from Shenzhen Nanotech. Port. Co. Ltd., China. Commercially available T700S carbon fibers (12 K, 1.78 g cm^{-3}), purchased from Japan Toray, were used as reinforcing fillers. 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.

2.2. Fabrication of multi-sized carbon fibers

First, carbon fibers were refluxed by acetone in Soxhlet apparatus at 80 °C for 24 h to remove the commercial sizing. The pretreatment of CF tows is to exclude commercial sizing clustering effect on CF, which could help to obtain a dispersion of CNTs in the small inter-fiber-spaces of CF bundles. Then CNTs were dispersed in ethyl alcohol and sonicated for 2 h to form a stable suspension of 0.3 mg ml^{-1}, which was a relatively low concentration [4,19,31]. Ethanol was selected as the dispersion medium because of its non-toxic character and good dispersion result. After that, the virgin CF tow was sized with a self-made device, as shown in Fig. 1. The virgin CF tow continuously passed through the sizing agent suspension and was wound up on a roller after drying using a heating oven. During the sizing process, excess suspension was removed by a tensioner. The take-up speed was maintained slow enough to obtain good wetting of the fibers. The contents of CNTs on CF surface were controlled by numbers of sizing treatment, thus triple sized-CF, quintuple sized-CF, septuple sized-CF and nonuple sized-CF were obtained. Afterward, the fibers were carefully kept from disturbance of strong airflow and physical touch before molding into composites.

2.3. Preparation of composite samples

The procedures of the preparation of unidirectional carbon fiber composites were as follows: (1) CF tows were laid up along the fiber axial orientation and put into the grooves of mold, and the fiber volume fraction of composite was kept at about 45%. (2) Epoxy resin, harder and accelerant were mixed well in a weight ratio of 100:70:1, then the mixture was degassed in vacuum oven at 60 °C for 0.5 h. (3) The prepared mixture was pressed into the mold under the pressure of 0.1 MPa using resin transfer molding method. (4) The composites were cured in an oven according to a curing step at 90 °C for 3 h, 120 °C for 3 h and 150 °C for 5 h. After curing, the samples were cooled naturally to room temperature.

2.4. Characterizations

Surface topography of carbon fibers and fracture surface of composite specimens were detected using SEM (Hitachi S-4800, Japan). All the SEM samples were coated with a layer of gold before test to improve conductivity.

To assess the influence of sizing process on interfacial properties, the short beam shear tests and flexural tests were carried out according to JC/T773-2010 and ASTM D790-03 standards, respectively. All tests were carried out at room temperature and the final values were calculated as averages of five specimens for each composite. Both tests were performed in a universal testing machine (Instron 3369, USA).

The interfacial microstructures of composites were studied by EDS (JEOL JSM-5900LV) equipped on SEM and f-AFM (CSPM 5500, China). The former is for carbon element distribution in the interface layer of composites and the latter is for the modulus distribution. To reduce errors caused by the rough surface of samples and accurately detect the structure of the interfacial layer, the cross-sections of composite specimens were polished using sand paper and Cr_2O_3 suspension respectively, followed by washing with acetone in ultrasonic and drying.

3. Results and discussion

3.1. Surface topography of carbon fibers

The surface morphology changes of the carbon fibers after sizing were verified by the SEM, and the results were shown in Fig. 2. Smooth surface with some sizing polymer and pollutants of as-received CF could be seen in Fig. 2a. After desizing, the virgin CF represented a smoother surface with some superficial grooves distributed along the axis (Fig. 2b), which indicated that the commercial sizing had been removed.

As could be seen, CNTs were introduced and randomly deposited on the surface of CF via sizing treatment. After triple sizing treatment, only a small amount of CNTs were adsorbed to CF surface. With the increase of times of sizing treatment, the contents of CNTs on fiber surface increased (Fig. 2d–f), which meant that controlling of CNTs content at interface was realized by regulation of times of sizing processes. However, when sizing treatment exceeded five

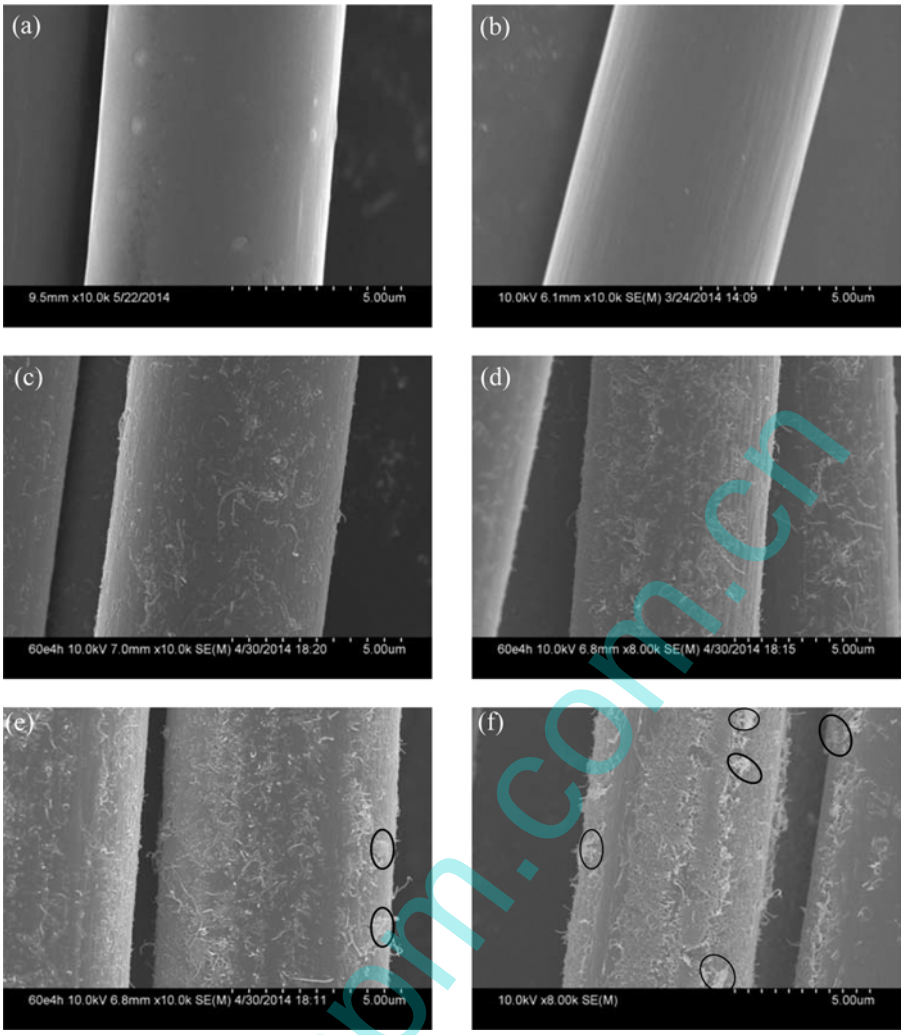

Fig. 2. Surface morphology of (a) as-received CF, (b) virgin CF, (c) triple sized-CF, (d) quintuple sized-CF, (e) septuple sized-CF, and (f) nonuple sized-CF.

times, CNT agglomerations were observed (marked by circles), as shown in Fig. 2e and f, which might affect the improvement of interfacial properties.

3.2. Mechanical properties of composites

Interlaminar shear strength (ILSS) is one of the most important interfacial properties for composites [16,32]. To investigate the effect of sizing treatment on interfacial properties, three-point short beam shear method was carried out to evaluate the effects of CNTs sizing. As shown in Fig. 3, the ILSS values of all kinds of composites were dependent on the quantity and distribution of CNTs in the interfacial regions. Repetition of sizing processes led to a gradual increase in the ILSS values and the quintuple sized-CF/epoxy composites showed a maximum ILSS value (75.06 MPa), with an improvement of 13.45% compared to virgin CF composites. This result indicated that the toughening of interface played an important role in transferring stress uniformly and increasing the resistance to interfacial shear debonding [33]. However, a further increase of times of sizing treatment led to a decline in interfacial properties. That fact should be related to the CNT agglomerations in the interfacial region (as shown in Fig. 2e and f), which served as localized defects and stress concentration sites and resulted in deterioration of interfacial strength [32].

The flexural tests were carried out to assure the effect of CNTs on the mechanical properties of composites. Results of flexural

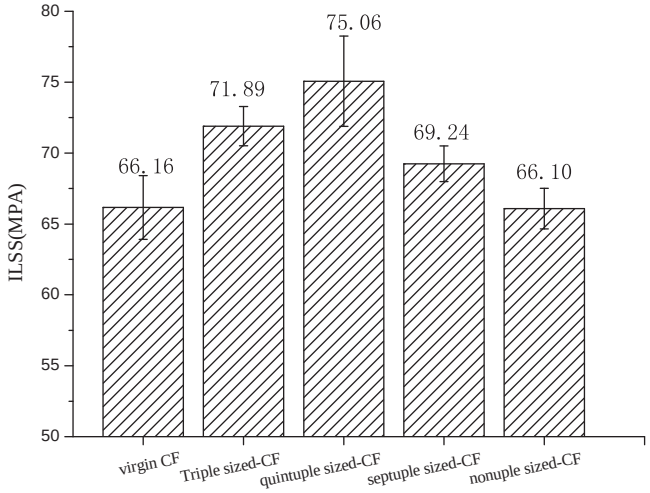

Fig. 3. Interlaminar shear strength of composites with multiple sizing treatments.

strength and flexural modulus were shown in Fig. 4. The variation trend of flexural strength with sizing times was coherent with the ILSS results (shown in Fig. 3). This result demonstrated that the interfacial property also had vital influence on flexural strength. The quintuple sized-CF composites yielded the maximum

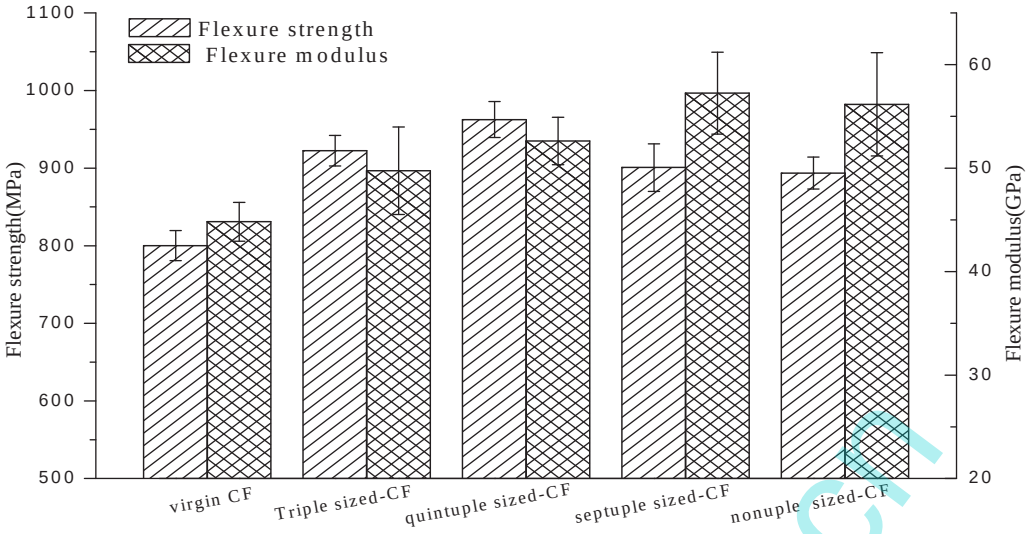

Fig. 4. Flexural properties of composites with multiple sizing treatments.

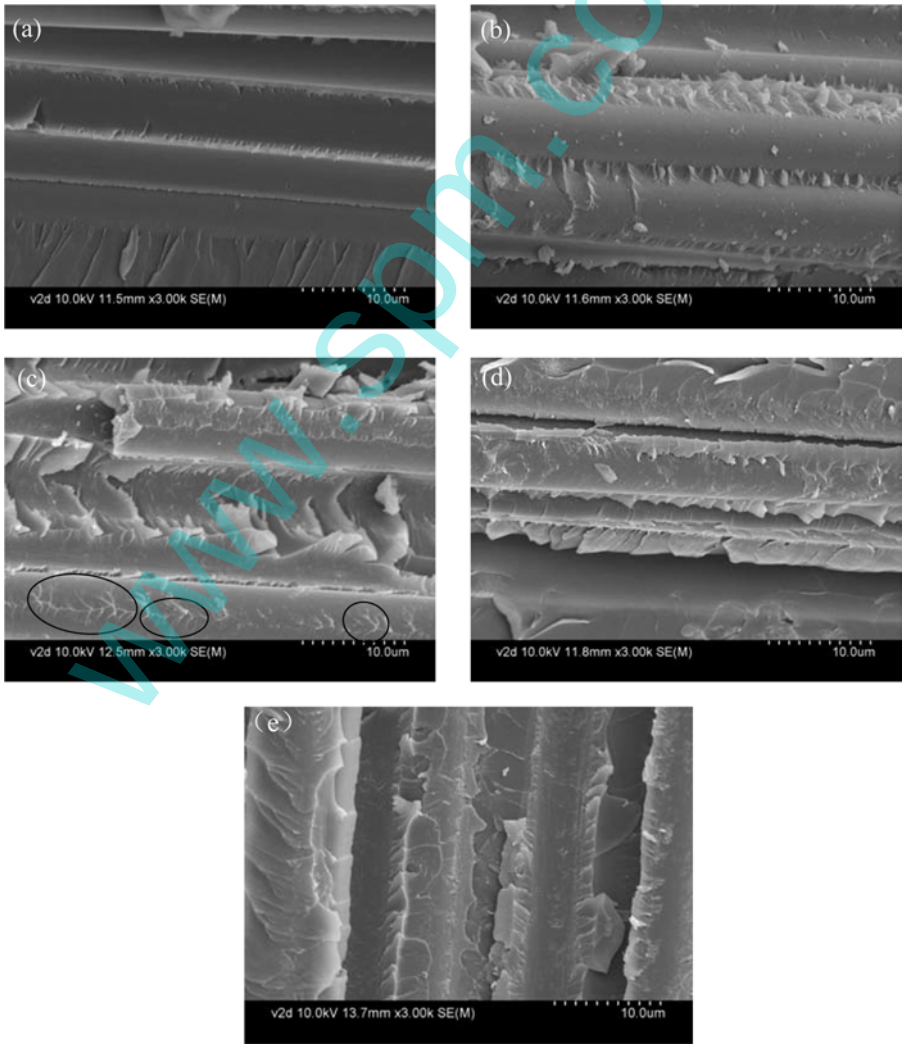

Fig. 5. Fracture surface of carbon fiber/epoxy composites: (a) virgin CF composites, (b) triple sized-CF composites, (c) quintuple sized-CF composites, (d) septuple sized-CF composites, and (e) nonuple sized-CF composites.

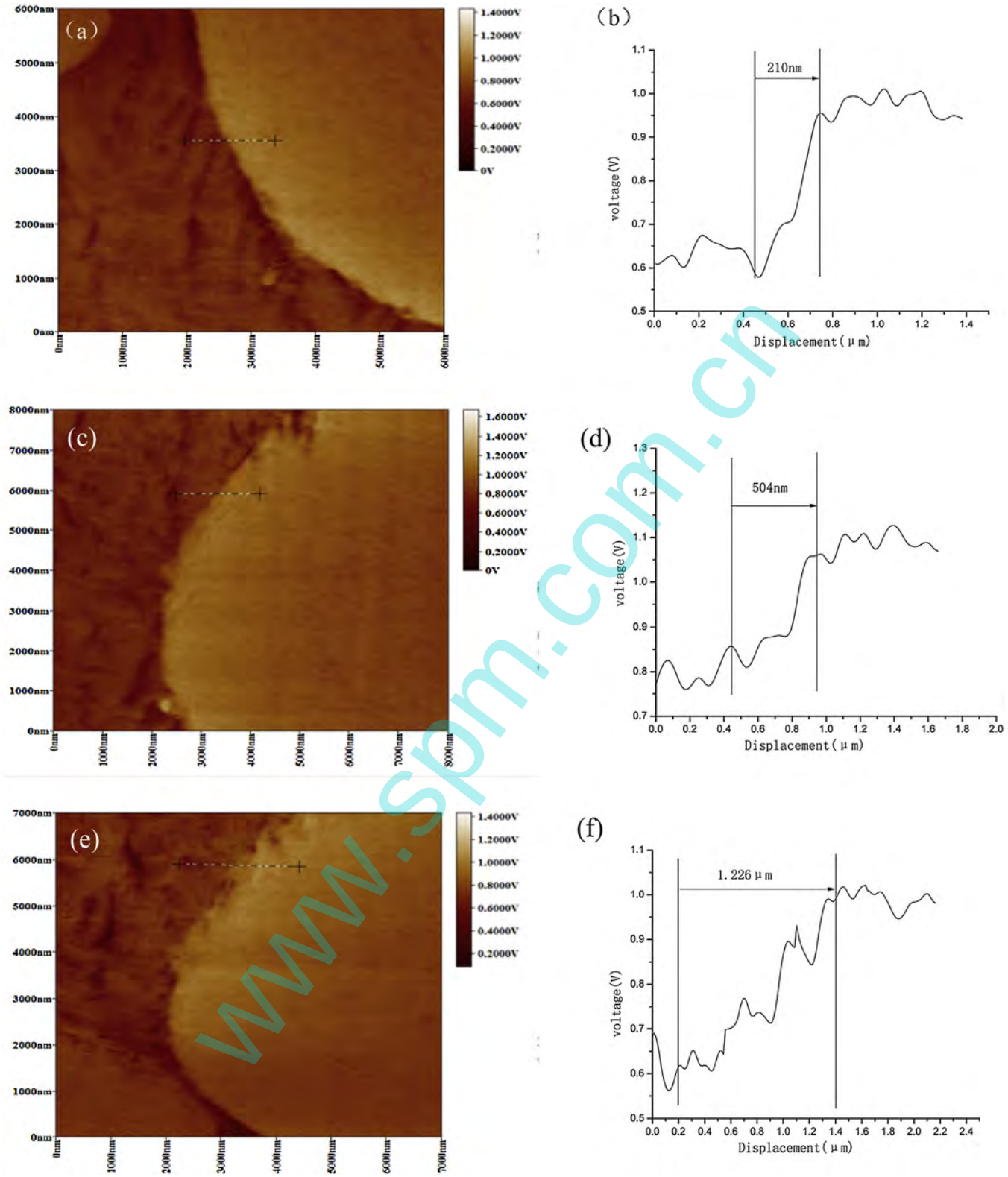

Fig. 6. Relative stiffness images and illustrations of stiffness distribution along the dotted line of cross-sections for (a and b) virgin CF composites, (c and d) triple sized-CF composites, and (e and f) quintuple sized-CF composites.

value (962.7 MPa), showing an increase of 20.31% compared to that of virgin CF composites. However, excessive CNTs in interfacial region caused decline of flexural strength. As for the flexural modulus, there were also obvious improvements in comparison with that of the pristine CF composites. Nevertheless, the flexural modulus continued growing after five-times sizing treatment and then seemed to remain constant in the next sizing processing of CF in the experiment, which might be due to the fact that the reinforced matrix increased the stiffness of composites and the stress concentration sites caused by CNT agglomerations hardly went against the stiffness of composites at the initial stage of loading.

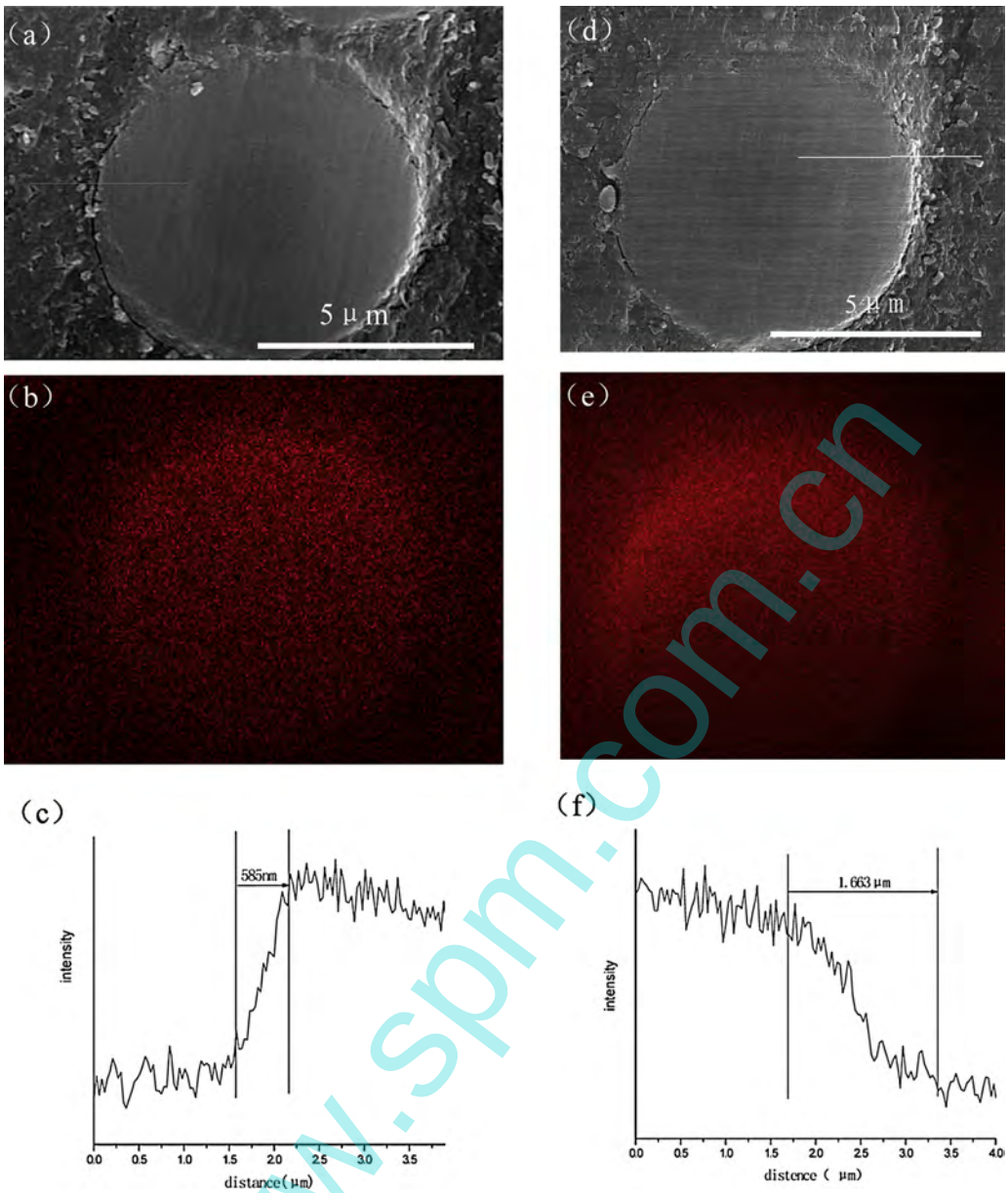

Fig. 7. Virgin CF composite cross-section: (a) SEM image, (b) distribution of carbon element (measured by EDS mapping scanning spectra), and (c) distribution of carbon element (measured by EDS linear scanning system) along the white line. Quintuple sized-CF composite cross-section: (d) SEM image, (e) distribution of carbon element (measured by EDS scanning spectra), and (f) distribution of carbon element (measured by EDS linear scanning system) along the white line.

3.3. Fracture surface of composites

Fracture surfaces of composites were detected by SEM after short beam shear tests to help understanding the enforcing mechanisms of CNTs. Fig. 5 represented SEM images captured from the fracture surface of composites. It could be observed that the shear debonding failure often occurred in interface region. For the fracture of virgin CF composites, the CF was rather clean and the matrix was comparatively neat, which indicated a weak interface. With the increase of times of sizing treatments, the matrix became rougher and more matrix attached to CF. Especially for the quintuple sized-CF composites (Fig. 5c), an amount of resin adhering to the carbon fiber surface could be seen (marked in circles), which was an evidence of a stronger interphase. This was related to the good dispersion of CNTs in interfacial region which resulted in increased modulus of matrix around CF, then the reinforced interphase contributed to stress transfer and damages started to occur at matrix. However, when sizing treatment exceeded five times, the CF became cleaner but the matrix still remained rough. This phenomenon showed that agglomerated CNTs reinforced matrix could fall off the fiber surface easily during loading, resulting in poor interfacial properties. But some CNTs could go into the matrix around the CF during molding, which could tough the matrix.

3.4. Microstructure of interfacial phase and reinforcing mechanism

The inertness and lack of reactive functional groups of CF decided that there was little chance that chemical bonding could form between CF and CNTs. Moreover, after sizing treatment, most of CNTs were lying on the fiber surface and the short CNTs may have little influence on increasing mechanical interlock between CNTs and matrix. Therefore, there is limitation to explain the specific reinforcing mechanisms in our work by chemical bond and

wetting theory. In our work, during the composite molding, some CNTs dropped from fiber surface and dispersed into matrix and a transition interface layer which has gradient properties between fillers and matrix might be formed. Herein, the interface transition layer could be built with CNTs sizing treatment compared to grafting [34] or in situ growth [10] which firmly attached CNTs on CF surface with strong bondings. This interface layer may eventually be beneficial to decrease stress concentration and raise the mechanical properties of composites [35–37]. To verify the introduction of transition interface layer and change trend of interfacial structure brought by sizing treatment, the interfaces of virgin CF composites, triple sized-CF composites and quintuple sized-CF composites were detected, in which CNTs were comparatively well-distributed.

Due to its micro-scale size, local mechanical properties of the interphase regions were characterized by the force modulation atomic force microscope (f-AFM). The cantilever tip of AFM indenting into the sample surface gives a description about the local modulus of sample surface. On the stiff areas of the sample surface, the deflection of cantilever is smaller, and on the soft areas larger. The relative stiffness value will be indirectly indicated by the voltage generated from the cantilever deflection [38,39]. To avoid resonance, tapping mode probe was adopted for its high inherent frequency. The intensity for force modulation driving amplitude was generally between 0.5 and 2 V and the frequency for probe vibration signal was between 20 and 40 kHz.

The force modulation images and illustrations of stiffness distribution along the dotted line in corresponding images obtained from the cross-section of the composites were shown in Fig. 6. In relative stiffness images, brighter area represents higher stiffness (namely, CF), and darker area represents matrix. As illustrated in Fig. 6a, apparent boundary between the fiber and matrix could be easily observed in cross-section of virgin CF composites, which was owing to the striking difference of modulus between fiber and matrix (Fig. 6b). This fact also illustrated the necessity to modify the interfacial microstructure. However, an interfacial layer about 210 nm thick was found due to slightly rough surface of virgin CF (Fig. 2b). Quite different from the virgin CF composites, as shown in Fig. 6c and e, the boundary between fiber and matrix became blurred because the modulus of interfacial area was increased, and it could be observed from the stiffness distribution curves of triple sized-CF and quintuple sized-CF composites (Fig. 6d and f) that a wider modulus transition region corresponding to the interphase existed. And more CNTs in interfacial region of quintuple sized-CF composites caused wider gradient transition layer (about 1.226 μm), which was thicker than that of the triple sized-CF composites (about 504 nm). The transition region could be attributed to the existence of interphase composed of CNTs and matrix. This interface region could act as a stress transfer medium to buffer and transfer load from matrix to carbon fibers uniformly, and delay the crack opening in failure mode [13,40,41]. Thus, the constructed gradient transition layer manifested itself at macro-scale as the improved ILSS and flexural properties of the composites.

EDS was further used to confirm the microstructure of the interface by scanning the distribution of carbon element on the cross-section of composites. Virgin CF composites and quintuple sized-CF composites were detected in detail. Both EDS linear scanning and mapping scanning tests were carried out and the results were shown in Fig. 7.

The distribution of carbon element across the cross-section of composites was manifested by EDS mapping scanning spectra. For the virgin CF composites (Fig. 7b), the outline of the CF was obvious and the amount of carbon element dropped suddenly along the white line (shown in Fig. 7a) from left to right in the virgin CF composite cross-section (Fig. 7c), which illustrated that the great difference of carbon content of the fiber and matrix. Whereas in the cross-section of quintuple sized-CF composites, it was difficult to distinguish boundary between fiber and matrix (Fig. 7e), indicating the presence of CNTs in interface. As could be seen in Fig. 7f, carbon element content decreased gradually from fibers to matrix, which demonstrated the gradient distribution of CNTs in the interface layer. The interphase thickness values were about 585 nm for virgin CF composites and 1.7 μm for quintuple sized-CF composites in Fig. 7, which were a little larger than that in Fig. 6b and f, and this might be due to difference of test methods or disparity of samples. Therefore, the existence of a gradient transition layer interface was demonstrated from another point of view by detection of the carbon element distribution in composite cross-section.

4. Conclusions

Sizing deposition process described herein provided a simple and continuous method to manufacture CF/CNTs/epoxy hierarchical composites in industrial scale. By studying the microstructure of the hierarchical composite interface using SEM/EDS and force modulation AFM, a gradient transition interphase was found, which could help to transfer stress uniformly. The content and distribution state of CNTs in interphase region affected the microstructures of interface, which thereby led to different interfacial properties of the composites. When CNTs were relatively uniformly distributed on the CF surface, interface thickness of gradient structure and mechanical properties of composites increased gradually with the increase of times of sizing treatment. Compared with the virgin CF composites, the quintuple sized-CF composites containing a relatively wider gradient interphase showed 13.45% improvement in interlaminar shear strength and 20.31% in flexure strength. However, excess sizing treatment would lead to deterioration of mechanical properties because of CNT agglomerations. Consequently, sizing treatment is an effective way to optimize interfacial microstructure, and then further improve interfacial properties of composites.

Acknowledgments

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