Original Article

Enhanced interfacial strength of carbon fiber/PEEK composites using a facile approach via PEI&ZIF-67 synergistic modification

Hansong Liu, Yan Zhao*, Na Li, Xiaoran Zhao, Xiao Han, Shuang Li, Wenkuo Lu, Kai Wang*, Shanyi Du

School of Materials Science and Engineering, Beihang University, Beijing 100191, China

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As a kind of metal-organic frameworks (MOFs) which possess large specific surface area and excellent thermal stability, zeolitic imidazolate framework-67 (ZIF-67) shows great application potentials because it can be synthesized in aqueous solutions at room temperature. In this work, we propose a synergistic strategy by taking advantages of polyetherimide (PEI) and ZIF-67 to enhance the interfacial strength of carbon fiber (CF) reinforced polyetheretherketone (PEEK) composites via a facile route. The bare CF is simply immersed into PEI solution and the aqueous solution of ZIF-67 precursors stepwise at room temperature to wrap PEI intermediate sizing layer and in situ grow ZIF-67 crystals. The surface morphology of CF indicates that regulating the concentration of PEI sizing agents can control the relative amount of ZIF-67 adhered onto CF surface. After modification, the tensile strength of single CF shows no deterioration and the interfacial shear strength (IFSS) of as-prepared modified CF/PEEK reveals an increase of 40.5%. Besides, the enhanced interfacial interaction mechanism might be ascribed to miscible feature of PEI with PEEK and rough structure from ZIF-67. This work may shed some light on establishing a facile and effective synthetic approach to modify CF and improve the performance of composites without degrading the mechanical property of pristine CF.

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1. Introduction

Continuous carbon fiber (CF) reinforced thermoplastic composites (CFRTP) have intriguing advantages including excellent stiffness and strength, high impact resistance, repeatable processing and recyclability [1–4], causing great concern as structural parts in aeronautic and aerospace industries [5,6]. However, an obvious obstacle to limit wider application of CFRTP is the weak interfacial properties [7,8] of interphase (the region between CF and resin) caused by hydrophobicity and chemical inertness of carbon [9–12]. As a result, the interface modification of CFRTP has attracted tremendous research interests both in academia and industry. In the present scenario, for high-performance thermoplastic polymers, a series of interface modification methods have been developed. Some

* Corresponding authors.
E-mails: jennyzhaoyan@buaa.edu.cn (Y. Zhao), wangkai@buaa.edu.cn (K. Wang).
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methods are trying to roughen the fiber surface and increase the contact area between CF and resin to enhance mechanical interlocking and achieve the improvement of the interfacial strength [13–16], while other chemical modification methods focus on increasing the active functional groups or introducing other substances with active functional groups, such as chemical grafting methods [17,18], coating treatments [19,20] and chemical activation methods [21,22].

For CF reinforced polyetheretherketone (CF/PEEK) composites, it is more appropriate to modify the interface by roughening the surface of CF. The reason can be concluded that the structure characteristic of PEEK macromolecular chain [23] determines that it cannot form a strong chemical interaction with CF surface. Moreover, the processing temperature of CF/PEEK composites can reach up to 380–400 °C, which is high enough to destroy the chemical bonds from modification. According to published literatures, the selection of physical modification methods, aiming to increase the surface roughness, proves to be an effective way to improve the interface bonding of resin and CF. Yamamoto et al. [24] and Sager et al. [25] discovered that grafting carbon nanotubes (CNTs) onto fiber surfaces via chemical vapor deposition (CVD) could provide CNTs with a radial orientation, which provided a possibility to offer a strong mechanical interlocking interaction favoring transverse reinforcement. Liu et al. [26] combined CF with graphene oxide (GO) sheets to prepare graphene aerogel (GA)-CF by one-step reduction and self-assembly of GO to maximize the surface area and surface roughness for enhancing the interfacial properties of composites. The interface shear strength (IFSS) of GA-CF reinforced composites revealed an improvement of 83.2%. Chen et al. [27] prepared poly(cyclotriphosphazene-co-4,4′-sulfonyldiphenone) nanotube (PZSNT)/CF hierarchical hybrid reinforcement to increase surface roughness of CF and finally enhanced the interfacial adhesion of composites. The IFSS of modified composites increased from 68.9 MPa to 87.1 MPa. However, the complexity of these methods may limit their further application.

Among these interface modification strategies of CFRTP, the usage of metal-organic frameworks (MOFs) to construct rough structure on CF surface has attracted our attention for their large surface area and high thermal stability [28–31]. Yang et al. [32] reported MOFs dense “armor” on the surface of fibers through fabricating UiO-66-NH2-Functionalized CFs. The IFSS was 44.1% higher than that of the pristine composites. However, most of MOFs were obtained under strict synthesis conditions, which reduced the possibility of their wide range of applications. In the class of MOFs, we found a kind of zeolitic imidazolate frameworks (ZIFs) called ZIF-67 (Co(Hmim)2, Hmim = 2-methylimidazole) had the potential to overcome the obstacles to application [33]. Qian et al. [34] reported the preparation of ZIF-67 nanocrystals in pure aqueous solutions at room temperature and this method increased the possibility of applying this material to interface modification. But up to now, using MOFs from this facile synthetic method to improve interfacial strength of CFRTP has rarely been reported.

Although introducing MOFs to interphase showed great potential, a serious problem of tightly anchoring nanoparticles on the surface of CF needed to be resolved. So effective surface pretreatment on CF surface was unavoidable. A great number of researches [21] have been done on CF surface treatment to increase surface energy, such as oxidation treatment, plasma treatment and gamma treatment. However, deterioration of fiber tensile strength was inevitable during these processes [35]. To maintain the tensile strength of CF, sizing [25,36] is a promising approach to modify the interfacial properties without compromising tensile properties. Many researches proved that sizing materials could protect CF from damage surface flaws or notches [37], and an increase of interfacial fracture toughness was achieved by choosing suitable thermoplastic resin as sizing agents on CF surface [38,39]. To obtain the optimized interfacial properties, the essential component of sizing agents should have the same or similar molecular structure with matrix, and it is also of great importance for sizing agents to exhibit inherent adhesion properties with CF and matrix. Hence seeking a kind of effective thermoplastics polymer as sizing agents which is suitable for CFRTP, has the advantage of working as the bridge to connect the inert CF with rough nanoparticles and improving interfacial combination of CF and matrix has become an essential task. As commercial sizing agents could not satisfy the requirement for interfacial enhancement, specific sizing agents need to be handled on the surface of CF for different matrix [39]. Hassan et al. [40] introduced polyetherketononeketone (PEKK) on the surface of activated CF. Due to hydrogen bond between PEKK and CF as well as good compatibility between PEKK and PEEK, interlaminar shear strength (ILSS) of modified CF/PEEK composites increased by 70%. Chiang et al. [41] coated polymeric acid (PAA) from different synthesis methods as sizing, and the effect ofimidization on the improvement of the interfacial bonding was investigated. As a kind of thermoplastic polymer which has the miscible feature to PEEK [42,43], polyetherimide (PEI) chains can spread to PEKK chains at high processing temperature and pressure. Giraud et al. [44,45] showed that PEI sizing on the surface of CF had the potential to improve interfacial adhesion of CF/PEEK composites, and complex interphase consisted between PEI and PEEK. Based on our previous work [46], the improvement of PEI sizing to interfacial properties of CF/PEEK composites was also be proved. On the other hand, the possible interactions including hydrogen bonds, π–π stacking and van der Waals forces between PEI and MOFs [47] provided their firm adherence.

In this research, we designed an interfacial modification method for CF/PEEK composites. ZIF-67 was introduced on the surface of PEI sizing-handled CF because of its facile synthetic condition and the capacity to be synthesized in situ on the surface of CF. The purpose was to establish a facile and effective synthetic approach of modified CF and improve the performance of composites without serious deterioration of fiber tensile strength. The crystal structure of synthetic ZIF-67 was determined and the chemical composition and morphologies of modified CF were investigated. After surface modification, the tensile strength of single CF and mechanical properties of interface were assessed. Based on the above testing results, the interfacial interaction mechanism was analyzed and discussed thoroughly. This new train of thought for interfacial modification is expected to be applied in a series of thermoplastic composites including CF/PEEK.
2. Experimental

2.1. Materials

CF (T700SC, 12K) was obtained from Japan Toray Industries, Inc. Polyetheretherketone (PEEK) powders were obtained from Changchun Jilin University Special Plastic Engineering Research Co., Ltd, China. Polyetherimide (PEI) was purchased from GE Plastics of America. Co(NO₃)₂·6H₂O and 2-methylimidazole were purchased from Guangzhou Jinhua Chemical Reagent Co., Ltd. and J&K Scientific Ltd. respectively. The solvent N-methyl-pyrrolidone (NMP) was purchased from Beijing Chemical Works. All reagents were of analytical grade.

2.2. Preparation of CF-PEI&ZIF

CF was refluxed by immersing them in acetone at 70 °C for 24 h to obtain the desired CF. FEI solution was obtained by dissolving PEI powders in NMP with robust magnetic stirring at 80 °C for 5 h. The concentration of solution was 0.001 g·mL⁻¹, 0.005 g·mL⁻¹, 0.010 g·mL⁻¹ and 0.025 g·mL⁻¹, respectively. The desired CF was pulled through PEI sizing agents. After drying, a solution of Co(NO₃)₂·6H₂O (145.5 mg, 0.5 mmol) in 5 ml of deionized water (component B) and a solution of 2-methylimidazole (3.284 g, 2 mmol) in 15 ml of deionized water (component B) were prepared. CF tows (pre-dispersed well at one end) were immersed in component B and ultrasonically treated for 20 min. Component A and component B were then mixed and stirred until well dispersed. The mixed system was held for 24 h at room temperature. Then the modified CF was rinsed thoroughly with ethanol and deionized water and ultrasonically treated. Subsequently, the modified CF was dried under vacuum at 70 °C overnight. The overall preparation procedure is shown in Fig. 1.

2.3. Physicochemical characterizations of ZIF-67 and CF

To research the crystal structure of ZIF-67, the X-ray diffraction (XRD) spectra were obtained by D/MAX2200 pc XRD instrument (Rigaku, Japan) using Cu Kα1 (λ = 0.154 nm) radiation. Thermal stability of ZIF-67 was recorded on TGA-50 thermogravimetric analyzer (Shimadzu, Japan) at a heating rate of 10 °C/min in air.

For modified CF, Fourier transform infrared spectroscopy (FTIR) measurements were performed using Nicolet 6700 FTIR spectrometer (ThermoFisher Scientific, USA). X-ray photoelectron spectroscopy (XPS) measurements were conducted on an ESCALab250Xi spectrometer (ThermoFisher Scientific, USA). Morphologies of modified CFs and fracture morphologies of CF/PEEK composites were observed using a scanning electron microscope (SEM, JEOL 7500F, Japan) with acceleration voltage of 20 kV, and elemental composition analysis was performed by energy dispersive spectroscopy (EDS). Atomic force microscope (AFM) images of modified CF were obtained using dimension icon atomic force microscope system (Veeco, USA).

2.4. Mechanical property measurements of CF and CF/PEEK

Tensile strength of single CF was measured by single-fiber tensile test [25,35,48], which was operated on a universal testing machine (Instron 5967, USA) according to ASTM D3379. The specimens were fixed on a tab, with a gage length of 20 mm (Fig. A.1) and the testing speed was 1 mm/min. The approach to obtain average tensile strength of single CF is described in the Supplementary Information (Appendix A).

The IFSS of CF/PEEK was evaluated through microbond test [49,50]. High-quality PEEK film was first processed using an extruding machine. A monofilament of CFs was installed on a C-shaped metal frame with both ends fixed, and the PEEK film which was cut into specific shape covered the monofilament. The frame was heated to 380 °C for several minutes. After the melt of PEEK and the formation of droplets, the sample (Fig. A.2a) was transferred to microbond test equipment. IFSS was measured through pulling off the PEEK resin droplets from the monofilament (Fig. A.2b). The fiber diameter, droplet size and blade position were kept consistent to eliminate the influences of these parameters on the test results [50]. The testing speed was 0.05 mm/min. The IFSS between CF/PEEK was calculated according to the following equation.

\[
\text{IFSS} = \frac{F_{\text{max}}}{\pi d_{\text{f}} L_{\text{e}}}
\]

where IFSS is the interfacial shear strength (MPa), \(F_{\text{max}}\) is the maximum force (μN), \(d_{\text{f}}\) is the average diameter of CF (μm) and \(L_{\text{e}}\) is the embedded length of microdroplets (μm) [27].

3. Results and discussion

3.1. Characterizations of ZIF-67

ZIF-67 was prepared in deionized aqueous solutions at room temperature, with an average size of approximately 280 nm. The XRD pattern (Fig. 2a) matched well with the simulated as well as the published pattern, demonstrating that the crystal was pure-phase ZIF-67 materials [33,34]. SEM image (Fig. 2b) revealed that the particles were nanocrystals with truncated dodecahedra shape (the inset is schematic model), which matched well with the published results [51]. To investigate the thermostability of ZIF-67, it was heated at designed processing temperature of CF/PEEK composites. TGA curve (Fig. A.3a) showed that no obvious weight loss (less than 5%) was observed before 380 °C. Moreover, from SEM image of ZIF-67 after this thermal treatment (Fig. A.3b), it is clearly found that the crystal structure of ZIF-67 was still remained (the inset is schematic model). The slight folding phenomenon of sample surface may be beneficial to the formation of rough structure. The outstanding thermostability of ZIF-67 provided possibility for its application to CF/PEEK interfacial modification.

3.2. Physicochemical characterizations of modified CF

FTIR spectrum was employed to analyze the functional groups of ZIF-67, as shown in Fig. 3a. The band at 2930 cm⁻¹ should
Fig. 1 – Schematic illustration for the formation process of CF-PEI&ZIF.

Fig. 2 – (a) As-synthesized and simulated XRD patterns of ZIF-67; (b) SEM image of ZIF-67 obtained using aqueous solutions as solvent.

Fig. 3 – FTIR spectra of: (a) ZIF-67, (b) CF, CF-PEI and CF-PEI&ZIF.
be ascribed to the aliphatic C–H stretch vibration. The C=N stretching vibration was observed at 1575 cm⁻¹. The peaks corresponding to the plane vibration of imidazole ring located at 1409 cm⁻¹ and 1307 cm⁻¹ were found in the spectrum. In addition, there were symmetrical stretching vibration at 1140 cm⁻¹ and out of plane vibration of imidazole ring in the range of 500–800 cm⁻¹. More importantly, the peak at 422 cm⁻¹ corresponding to the Co-N indicated that ZIF-67 has been successfully synthesized. 

The surface chemical composition of unmodified CF, CF-PEI and CF-PEI&ZIF was studied by XPS. The concentration of PEI was 0.010 g·mL⁻¹. The compositions of carbon, oxygen, and nitrogen were detected at around 284.8 eV, 532.5 eV and 400.4 eV for all kinds of CF (Fig. 4a). However, CF-PEI&ZIF showed a stronger peak in the N 1s compared to unmodified CF and CF-PEI, indicating a significant increase of nitrogen element on fiber surface. Particularly, the appearance of higher binding energy peak at 781.2 eV for CF-PEI&ZIF, which should
be assigned to Co 2p, also proved the existence of ZIF-67 on fiber surface. To estimate the chemical states of Co, the spectrum of Co 2p peak was fitted for further analysis in Fig. 4b. Two apparent peaks with binding energy of 781.1 eV and 796.8 eV can be observed in the XPS peak for Co 2p, corresponding to Co 2p$_{3/2}$ and Co 2p$_{1/2}$, respectively. The two small and indistinctive peaks at 784.9 eV and 802.4 eV were consistent with the results reported in the literature [32], representing Co$^{2+}$ shakeup satellite peaks. The C 1s peaks of XPS spectra of unmodified CF (Fig. 4c), CF-PEI (Fig. 4d) and CF-PEI&ZIF (Fig. 4e) were fitted into several peaks including the C–C (284.8 eV), the C=O (286.4 eV), the C–C=O (288.3 eV) and the C–N (285.8 eV). Obviously, the C 1s of CF-PEI&ZIF exhibited the appearance of the C–N peak, which verified the successful growth of ZIF-67 on CF surface.

3.3. Surface microstructures of modified CF

The surface morphology of CF after modification was examined by SEM. The mass fraction of PEI sizing agent was first
measured, and the result was shown in Fig. 5a. The color of solution was darker with the increase of PEI concentration (Fig. 5b). In our previous research [46], the ability of PEI to form perfect films was experimentally confirmed. Compared with bare CF surface which was relatively smooth (Fig. 6a), PEI sizing could modify CF with a layer of film covering the surface. The thickness of film increased with the addition of PEI concentration and grooves on the surface of CF reduced (Fig. A.4). Furthermore, the possible interactions between ZIF-67 and PEI [47] provided their strong adherence. Hence it is speculated that the amount of ZIF-67 anchored on CF surface could be regulated by adjusting the concentration of PEI sizing agents. In this research, we chose a facile synthetic strategy to in situ grow ZIF-67 on CF surface. Specifically, CF was immersed in component B and then mixed with component A. The disadvantage of this method was the difficulty in controlling the concentration of the product by altering the amount of components added, because merely changing the ratio of components and synthesis condition brought a series of problems such as the dimensional instability of particles and the change of crystal structure [34]. To overcome this obstacle, PEI sizing agent was used as the adhesive layer to introduce ZIF-67 effectively, which was aiming to construct undulating structure on the surface of CF at the meantime. The content of ZIF-67 on CF surface was regulated through changing the PEI concentration. Besides, good compatibility of PEI and PEEK could also optimize the interphase performance, providing a positive synergistic effect.

The observation of the surface morphology of modified CF proved our prediction. As shown in Fig. 6, the content of ZIF-67 increased obviously with the addition of PEI concentration at the same synthesis condition. In Fig. 6b, it can be seen that inherent grooves on CF surface were observed when the concentration of PEI solution was 0.001 g·mL\(^{-1}\) due to the thin layer of sizing agents. ZIF-67 distributed on CF surface but particles were sparse and discontinuous. In Fig. 6c, more ZIF-67 particles were presented on CF surface at higher PEI concentration (0.005 g·mL\(^{-1}\)), but uncovered parts could still be observed, demonstrating that the distribution of ZIF-67 on the surface of CF was discontinuous. Some grooves on the uncovered parts of CF surface could be observed, which was less obvious than CF in Fig. 6b. Fig. 6d indicated that ZIF-67 covered evenly on CF surface and a layer of ZIF “armor” was formed [32] at PEI concentration of 0.010 g·mL\(^{-1}\). The covering of the “armor” presented a problem about investigating the surface state of CF in this situation. Therefore, PEI sizing CF without ZIF-67 was prepared and the surface morphology of sized CF (Fig. A.4a) showed that there were still shallow grooves on the

Fig. 7 – EDS mapping scanning images of CF-PEI&ZIF: (a) SEM image and mapping image of (b) C element, (c) Co element, (d) Pt element.
surface of CF. In Fig. 6e, the concentration of PEI solution was raised to 0.025 g·mL⁻¹ and the surface morphology was similar to that in Fig. 6d. The surface morphology of CF (without ZIF-67) treated with the same PEI sizing agent concentration was observed (Fig. A.4b). It was found that no obvious groove structure could be observed on the surface of CF, and the reason could be attributed to the higher concentration of PEI sizing agent and the formed surface film layer, which concealed the inherent undulating morphology of the CF surface. Moreover, the test results from EDS mapping scanning spectra (Fig. 7) proved the distribution of Co element (shown in Fig. 7c) at PEI concentration of 0.010 g·mL⁻¹, which intuitively validated the existence of ZIF-67 on CF surface.

AFM images corresponded well to SEM results. The surface of desized CF showed obvious shallow groove structures, as shown in Fig. 8a. Some granular discontinuous undulating structure was observed after treating with PEI (c_{PEI} = 0.001 g·mL⁻¹) and ZIF-67, as shown in Fig. 8b. In Fig. 8c, the amount of granular undulating structure increased but it was still discontinuous on PEI (c_{PEI} = 0.005 g·mL⁻¹) and ZIF-67 synergistically modified CF surface. At much higher PEI concentration (c_{PEI} = 0.010 g·mL⁻¹), Fig. 8d illustrated that the uniformly covered “armor” appeared on modified CF surface and the “armor” still existed at the PEI concentration of 0.025 g·mL⁻¹ (Fig. 8e). It may be deduced that the “armor” structure constructed by this method had an impact on CF/PEEK interfacial strength.

Fig. 8 – AFM images of CF-PEI&ZIF at PEI concentration of (a) 0 g·mL⁻¹, (b) 0.001 g·mL⁻¹, (c) 0.005 g·mL⁻¹, (d) 0.010 g·mL⁻¹, (e) 0.025 g·mL⁻¹.

Fig. 9 – Micro interfacial shear strength results of CF/PEEK composites.

3.4. Mechanical property measurements of CF and CF/PEEK

As shown in the Supplementary Information (Appendix A), tensile strength of single CF increased slightly from 4369.92 MPa to 4411.92 MPa (c_{PEI} = 0.010 g·mL⁻¹), which illustrated that as-proposed interfacial modification method could
The IFSS results of different CF/PEEK composites were presented in Fig. 9. Blue bars in the histogram showed that IFSS increased by 40.5% from 46.4 MPa for bare CF to 65.2 MPa for PEI&ZIF-67 modified CF \((c_{\text{PEI}} = 0.010 \text{g.mL}^{-1})\). The result indicated that more effective interfacial interaction was achieved for PEI&ZIF-67 synergistically modified CF. Specifically, IFSS raised with the addition of PEI concentration (from 0 g.mL\(^{-1}\) to 0.010 g.mL\(^{-1}\)), but the tendency altered at the PEI concentration of 0.025 g.mL\(^{-1}\). The similar phenomenon occurred in other research work \([17,52]\) and thus we deduced that the aggregation of overmuch ZIF-67 particles in interphase caused local stress concentration, which was not conducive to energy dissipation and decreased the interfacial strength of composites.

The information from Fig. 9 also revealed the individual effect of ZIF-67 and PEI in interface modification. Without PEI sizing, IFSS of composites with ZIF-67 modified CF slightly increased from 46.4 MPa to 55.0 MPa (the first blue bar), by 18.4%. This situation could be due to the difficulty to establish effective connections between ZIF-67 and bare CF surface because of the chemical inertness of CF \([9,11,53]\), which greatly reduced the effectiveness of interface modification. On the other hand, without ZIF-67, the effect of PEI sizing on IFSS was also investigated. As shown in Fig. 9 (orange bars), PEI sizing brought a positive influence on IFSS. From experimental results and our previous research \([46]\), the maximum IFSS value obtained based on this modification technique was 49.4 MPa, increases by only 6.5% from 46.4 MPa for the bare
The result proved the effectiveness of this sizing modification method [44,45]. However, the strengthening effect from the increase of PEI concentration was less than that from the introduction of ZIF-67. In conclusion, through this synergistic modification method, the full advantages of PEI and ZIF-67 can be taken to achieve better interface strengthening effect.

To further understand the mechanisms for such enhancement, the fractured morphologies of CF after microbond test were researched by SEM. In Fig. 10a, a smooth fracture surface appeared on PEEK microdroplet, and no residual resin could be observed, both of which illustrated poor interfacial interaction between bare CF and PEEK. As a result, relatively low IFSS value was obtained. In Fig. 10b,c, with the increase of PEI concentration (from 0.001 g·mL⁻¹ to 0.005 g·mL⁻¹), it was observed that the fracture surface became more rugged, and more residual bulges of PEEK resin were discovered on CF surface. In Fig. 10d (cPEI = 0.010 g·mL⁻¹), these characteristics were showed more obviously. From these phenomena we presumed that rough structures constructed on CF surface caused considerable resistance against PEEK microdroplet during the debonding process, which could also be evidenced from the enhancement in IFSS value. These results suggested that PEI and ZIF-67 provided strong mechanical interlocking and interfacial adhesion for enhanced interfacial strength. In Fig. 10e, due to the high PEI concentration (0.025 g·mL⁻¹), the granular undulating structure of fiber surface can be clearly observed. This phenomenon revealed that too many ZIF-67 particles prevented the contact of sizing layer and matrix, thus the descend of IFSS value occurred.

The possible bonding mechanism of modified CF/PEEK is shown in Fig. 11. For PEEK, due to the miscible feature of PEI, chains of matrix resin can spread to sizing layers during processing, which provides an effective stress transfer system to achieve uniform distribution of stress between CF and PEEK. At the same time, rough structure from ZIF-67 “armor” restraints the extension of microcracks and turn the direction of microcracks to the interphase [54]. Due to the two factors above, cracked PEEK resin remained on the fiber surface after debonding. As a result, the interfacial strength of composites is enhanced after interface modification. Some of the estimations have been approved by SEM images and IFSS results as mentioned above.

### 4. Conclusions

In summary, a facile and effective method using PEI&ZIF-67 synergistically modified CF to enhance the interfacial strength of CF/PEEK composites is proposed. In this synergistic strategy, PEI acts as thermoplastic polymer sizing agents and ZIF-67 constructs rough granular undulating structure on the surface of CF. As a facile way of interface modification, the preparation of ZIF-67 is completed in aqueous solutions at room temperature. Physicochemical characterizations and surface microstructures of modified CF show that ZIF-67 forms a layer of “armor” at the optimized PEI concentrations. The tensile strength of single CF maintains, because microdefects on CF surface can be healed through sizing. More importantly, IFSS increases by 40.5% from 46.4 MPa for bare CF to 65.2 MPa for PEI&ZIF-67 modified CF at PEI concentration of 0.010 g·mL⁻¹. The fractured morphologies of CF after microbond test suggest better interfacial properties of composites by introducing PEI and ZIF-67 to CF/PEEK interphase. The miscible feature of PEI with PEEK and rough structure from ZIF-67 might be two main factors resulting in the enhanced interfacial properties of CF/PEEK composites. Due to the ease of implementation and universality of this method, the novel interface modification is expected to be applied in a series of thermoplastic composites.

### Declaration of interests

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.

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### Appendix A. Supplementary data

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