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Enhanced interfacial interactions of carbon fiber reinforced PEEK composites by regulating PEI and graphene oxide complex sizing at the interface

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ABSTRACT

The interfacial interactions and bonding of carbon fiber (CF) reinforced poly(ether-ether-ketone) (PEEK) composites is improved by applying polyether imide (PEI) and graphene oxide (GO) complex sizing at different ratios at the interface. The thermally stable polyether imide (PEI) and graphene oxide (GO) complex sizing is prepared and then coated on carbon fiber surfaces homogeneously. The sizing layer forms on the fiber surfaces, and multiple GO sheets are introduced successfully surrounding the carbon fibers. The surface morphologies of carbon fibers change distinctly with different GO contents. The interfacial shear strength (IFSS) increases from 43.4 MPa for bare fiber reinforced PEEK composites to 49.4 MPa for composites reinforced by carbon fibers coated with PEI only. However, a significant improvement is achieved when GO sheets are introduced to the CF surfaces, making the IFSS grow up to 63.4 MPa. Furthermore, the dynamic mechanical tests show that the normalized damping area results of carbon fibers coated with complex sizing decrease remarkably by about 50%. DMA results, interlaminar shear strength (ILSS) test and flexural test results are in agreement with each other, suggesting better interface bonding of composites by applying PEI and GO complex sizing. Besides, the interfacial interaction mechanism in modified composites is proposed. The enhanced interfacial performance is caused by the positive effect of complex interface layer.

1. Introduction

In recent years, due to the increasing demands for excellent impact toughness [1,2], repeatable processing and recyclability [3,4], continuous carbon fiber reinforced thermoplastic composites have drawn great attention in a variety of high-performance structural applications to replace the conventional thermoset composites. However, the long molecular chains of thermoplastic matrix make the interface formation with fibers different from thermoset matrix. For thermoplastic matrix, their long and inert chains are very difficult to form any chemical bonding with carbon fibers. Obviously, the chemical bonding plays a crucial role in interfacial bonding of thermoset composites [5,6]. It means that the strong interfacial interactions and bonding may be a puzzled issue for fibers and thermoplastic matrix. This notable problem has attracted great interest in developing new concepts for enhancing the interfacial bonding of continuous fiber reinforced thermoplastic composites, for example, the ozone or plasma treatment on fiber surfaces [7–9], the modification of matrix [10,11], the introduction of coupling agents [12,13] or nano particles [14], increasing the fiber surface roughness [15,16] and other multiscale modification methods [17]. However, not all of the above methods are effective in improving interface bonding. Some of them could damage the fibers or only be realized in lab, which limits the application for industrial preparation and production.

Furthermore, for polyphenylene sulfide (PPS), poly(ether-ether-ketone) (PEEK) and other high-temperature thermoplastic polymers widely applied in aerospace, their interfacial problems are more intractable due to the high processing and operating temperature [18]. Not only do fibers have troubles in forming strong interfacial chemical or physical bonding with thermoplastic polymers, but also the surface sizing (epoxy, polyurethane etc.) of commercial fibers may be degraded during processing [19], which will weaken the interfacial bonding. All of these observations

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underline the importance of tailoring the intrinsical microstructure of fiber surfaces directly or applying thermally stable sizing on fiber surfaces to enhance the bonding of fiber and high-temperature thermoplastic matrices. Li [20] reported the interfacial study on the ozone and air-oxidation-modified carbon fiber reinforced PEEK composites. The maximum interfacial shear strength (IFSS) could grow from about 35 MPa for untreated fibers to about 55 MPa for ozone treated fibers. However, it is difficult to be applied to the continuous production. Wenbo et al. [21] studied the improved interfacial bonding for CF/poly (phthalazinone ether ketone) (PPEK) composites by coating a thin PPEK film on carbon fiber surfaces. The results showed that the IFSS increased from 39.51 MPa for unsized carbon fiber (T700) reinforced PPEK composites to 51.49 MPa for resized composites. Chuang et al. [22] investigated the polyamic acid (PAA) with different molecular structures as sizing to increase the interfacial bonding of carbon fiber and PEEK, and Yuan et al. [23] improved the interfacial adhesion in CF/polyether sulfone (PES) composites through PAA sizing. The IFSS increased by about 20% to about 50 MPa. Nan et al. [24,25] had developed many methods to introduce the sizing layer on carbon fiber surfaces to increase the mechanical performance of high-temperature thermoplastic composites (Copoly(phthalazinone ether sulfone)s, PPBES). The results showed that the chemical and physical interactions had a great contribution to improving the interlaminar shear strength (ILSS) and flexural performance. Due to the miscible feature of PEI and PEEK [26,27], PEEK chains can diffuse into PEI chains easily at high processing temperature and pressure. Giraud et al. [18,28] reported a concept that the PEI sizing on the carbon fiber surfaces could improve the interfacial adhesion of CF/PEEK composites. The complex interface layer may be made of PEI and PEEK. They did not further investigate the actual interfacial bonding performance in their study.

On the other hand, introducing some nanoparticles can increase the surface roughness and the resistance to crack propagation in composites. Patterson et al. [29] reported that the simple addition of ZnO nanoparticles on the surfaces can increase the roughness of fiber, and IFSS was observed to increase by 18.9% in epoxy composites. Besides, Yu et al. [30] investigated the enhancing effects of multi-walled carbon nanotubes (MWCNTs) on the interphase between epoxy matrix and carbon fiber. An increase of 26.3% in IFSS was achieved by incorporating 0.05 wt% MWCNTs into silane coating on the surfaces of carbon fiber. Zhang et al. [31] adopted graphene oxide to increase the interfacial bonding of carbon fiber and epoxy, and the IFSS increased by 70.9%. Furthermore, Yang et al. [14] described that the ILSS of carbon fiber reinforced PA6 composites increased only by introducing GO sheets, but it was very difficult for the GO sheets to be dispersed on the fiber surfaces homogenously in their study. They did not further investigate the interfacial enhancing effects. The introduction of nanoparticles at the interface of carbon fiber and thermoplastic matrix remains to be further developed. Besides, it is speculated that their enhancing effects and mechanisms at the interface in fiber reinforced thermoplastic composites shall be different from the thermoset composites. Based on the above research, it is a good choice to adopt the polymer with excellent compatibility with matrix as an adhesive to introduce nanoparticles. It is also speculated that the introduction of matrix-compatible polymer and nanoparticles is beneficial to improve the mechanical interlocking and molecular entanglement at the interface, showing a synergistic effect.

In our work, the thermally stable PEI and GO complex sizing is prepared and then coated on carbon fiber surfaces. The surface morphologies of carbon fiber after sizing are examined by SEM and AFM. The micro interfacial properties of modified carbon fiber reinforced PEEK composites are evaluated by the microbond test. The interfacial damping of composites has been revealed by dynamic mechanical method. Furthermore, the macro interfacial performance has been investigated by three-point short beam shear test and flexural test. Their fracture morphologies are also observed by SEM. Finally, the interfacial interaction mechanisms are developed, which contributes to future research on improving the interfacial interactions. It has potential application in improving interfacial performance during the manufacture of fiber reinforced high-temperature thermoplastic prepregs or composites in a production line.

2. Experimental

2.1. Materials

PEEK powders were obtained from Changchun Jilin University Special Plastic Engineering Research Co., Ltd, China. Polyether imide (PEI) was purchased from GE Plastics of America. Carbon fibers T700SC-12K were obtained from Japan Toray and desized totally. Fine graphene oxide (GO) was supplied by AECC Beijing Institute of Aeronautical Material. The ratio of carbon to oxygen is about 2 to 1. The solvent N-methyl-pyrrolidone (NMP, A.R.) was purchased from Beijing Chemical Works. The emulsifier Triton X-100 (C.P.) was obtained from Xilong Scientific company of China.

2.2. Preparation of sizing agent

PEI granules were dissolved in NMP with the magneton stirring at 80 °C for several hours. A homogeneous solution (0.01 g/ml) was obtained. GO was dispersed in PEI solution with GO contents of 0, 1, 2.5, 5, 7.5, 10 and 15 wt%, respectively. It can be defined as PEI + GO0, PEI + GO1, PEI + GO2.5, PEI + GO5, PEI + GO7.5, PEI + GO10 and PEI + GO15, respectively. In this work, the sizing agent was kept constant at about 1 wt% in the fiber sizing, and GO varies from 0 to 15 part per hundred of PEI.

2.3. Preparation of CF/PEEK composites

The bare carbon fibers were pulled through the PEI and GO complex sizing at a low extraction speed. And then, they were dried in IR heater at about 300 °C. They were pulled through the PEEK suspension (a well-dispersed mixture of PEEK, Triton X-100 and deionized water). The carbon fibers capsulated by PEEK powders were put into oven to remove residual solvents and consolidated to obtain CF/PEEK prepregs under pressure. After these prepregs had been cut into designed sizes, they were laid up in the unidirectional fiber orientation on a steel mold to prepare well-impregnated composites. Composite laminates were obtained with the final fiber volume fraction about 50%-53%. This process was illustrated in Fig. 1.

2.4. Microbond test for micro-interface behavior

Microbond test was carried out to determine the interfacial shear strength (IFSS) of the modified carbon fiber and PEEK. It could clearly reveal the effects of carbon fiber interface microstructure on bonding properties [32,33]. However, it was difficult for PEEK with high melting temperature to prepare microbond test samples. The method employed in this work was different from those have adopted in other work [34,35]. At first, PEEK resin was melt and extruded into film (thickness about 40 μm) by an extruder. PEEK film was cut into specific shape and then knotted around carbon fiber monofilament as shown in Fig. A.1 (Appendix A). Next, the

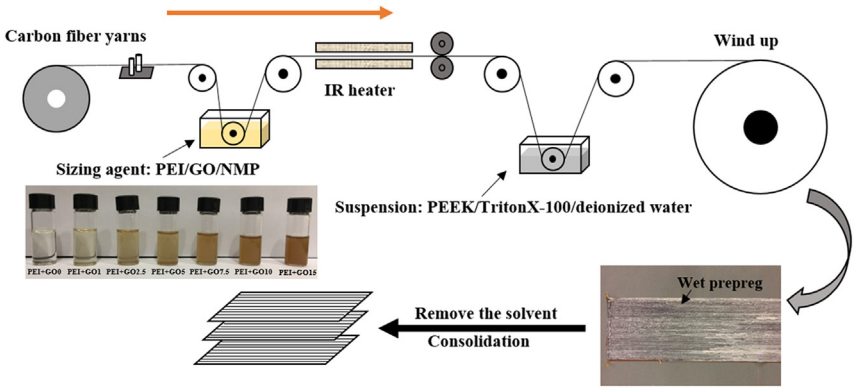


Fig. 1. Schematic illustration of the preparation of modified carbon fiber reinforced PEEK composites.

sample was put into a small nitrogen oven at a temperature of 400 °C for a few minutes. After that, the sample was removed from the oven and cooled down. In order to investigate the effects of hygrothermal conditions on interface bonding of modified carbon fiber and PEEK, the samples were soaked in the water (70 °C) for 72 h [23,36].

The sample was loaded at a speed of 0.05 mm/min. The IFSS, τ, was calculated based on the following equation.

$$\tau = \frac{F_{max}}{\pi d l} \quad (1)$$

where F_{max} is the maximum pull-out force, d is the fiber diameter and l is the embedded length of PEEK droplet.

2.5. Static and dynamic mechanical performance of composites

CF/PEEK laminates were employed to investigate their mechanical performance. The three-point short beam shear test was carried out according to ASTM D2344 standards (size: 12*4*2 mm) to determine the effects of PEI and GO complex sizing on the interlaminar and interfacial properties. The flexural test of CF/PEEK composites were performed according to the standard ASTM D7264. Dynamic mechanical measurements were done on a Mettler DMA system, at three-point bend mode at a heating rate of 5 °C/min at 1 Hz.

2.6. Other relevant characterization

Scanning electron microscopy (SEM, JEOL 7500F) was employed to investigate the microscopic surface and interface morphologies. Atomic force microscope (AFM) images of GO sheets and modified carbon fibers were obtained by a Multimode Nano4 in tapping mode. Thermal stability was recorded on a Thermogravimetric Analyzer (SHIMADZU TGA-50) at a heating rate of 10 °C/min in nitrogen.

3. Results and discussion

3.1. Basic features of GO

The SEM images of fine GO sheets are shown in Fig. 2a. They are easy to be dispersed in such polar solvents as water, NMP and DMF. A representative AFM image of GO can be seen in Fig. 2a, which reveals the presence of irregularly shaped sheets with thickness of about 1–1.5 nm. Some GO sheets are stacked during the actual sample preparation process. The size of GO mainly covers 0.5–3 μm. In Fig. 2b, the spectrum of GO confirms the presence of C-O (at 1073 cm^{-1}), O-C-O (at 1231 and 806 cm^{-1}), ketene C=O (at 1628 cm^{-1}) and carboxyl C=O (at 1720 cm^{-1}), O-H (the peak at 3419 cm^{-1}). A broad peak can be observed from 3700 to 2000 cm^{-1}, which is a clear feature of the presence of GO [37–39].

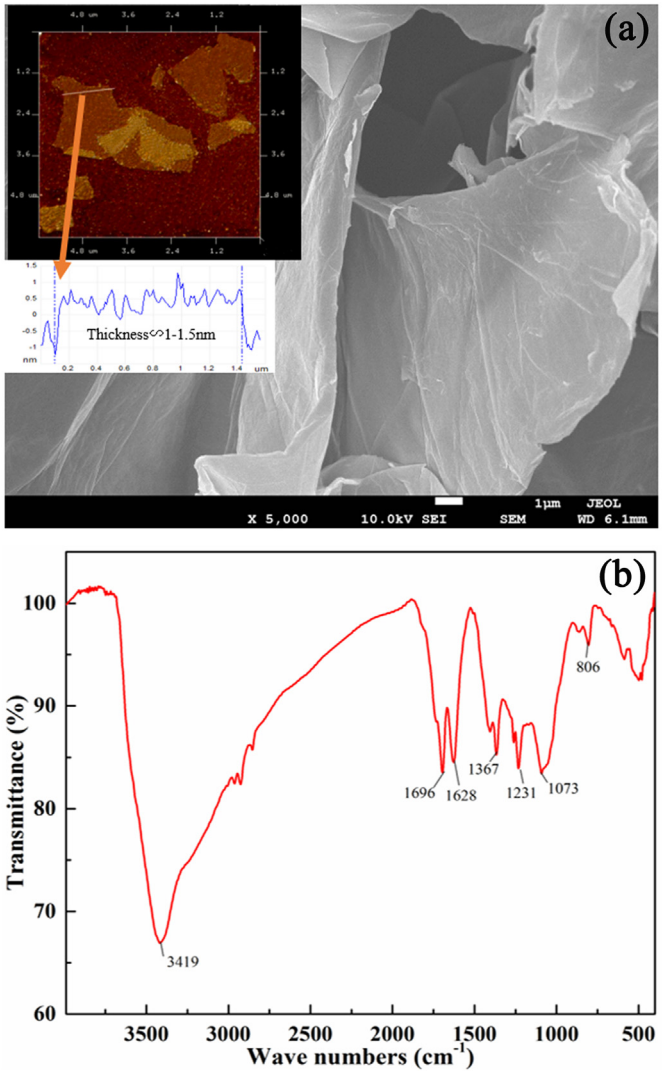


Fig. 2. Morphologies and IR spectrum of graphene oxide sheets: (a) SEM image of dry powder, AFM images of GO dispersed in water in the top left corner, (b) IR spectrum of GO.

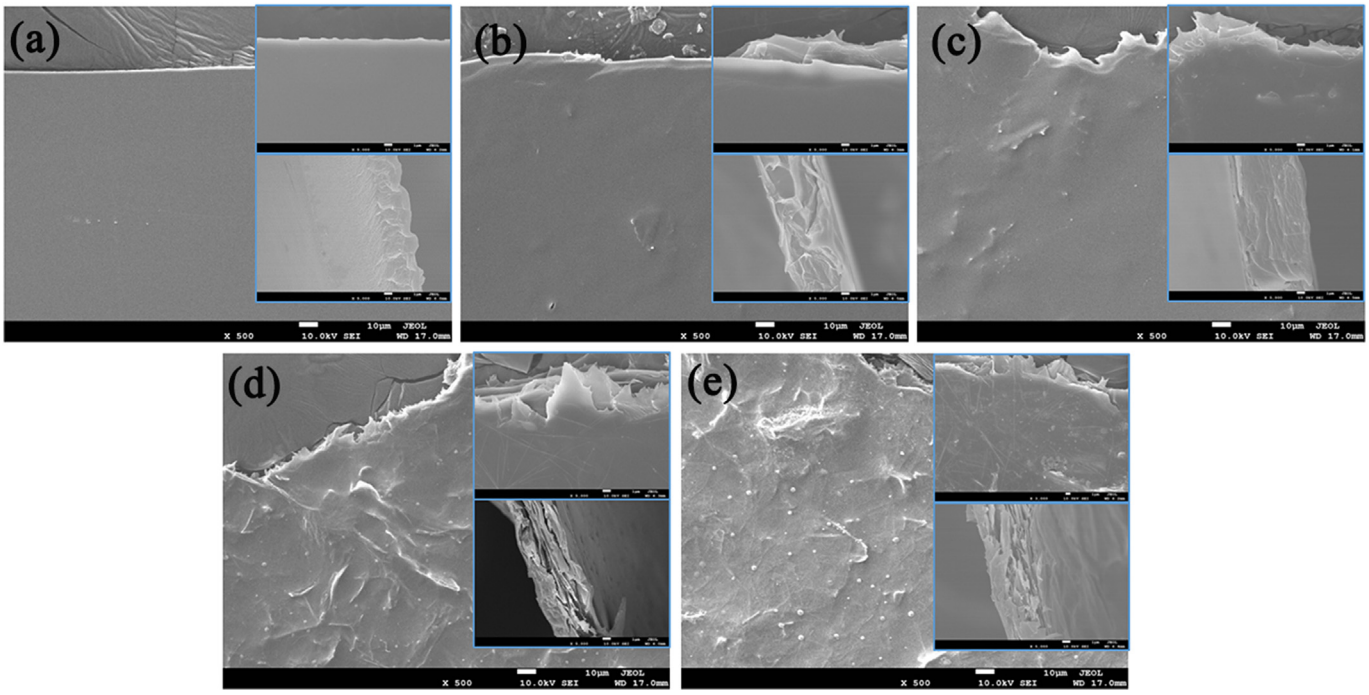
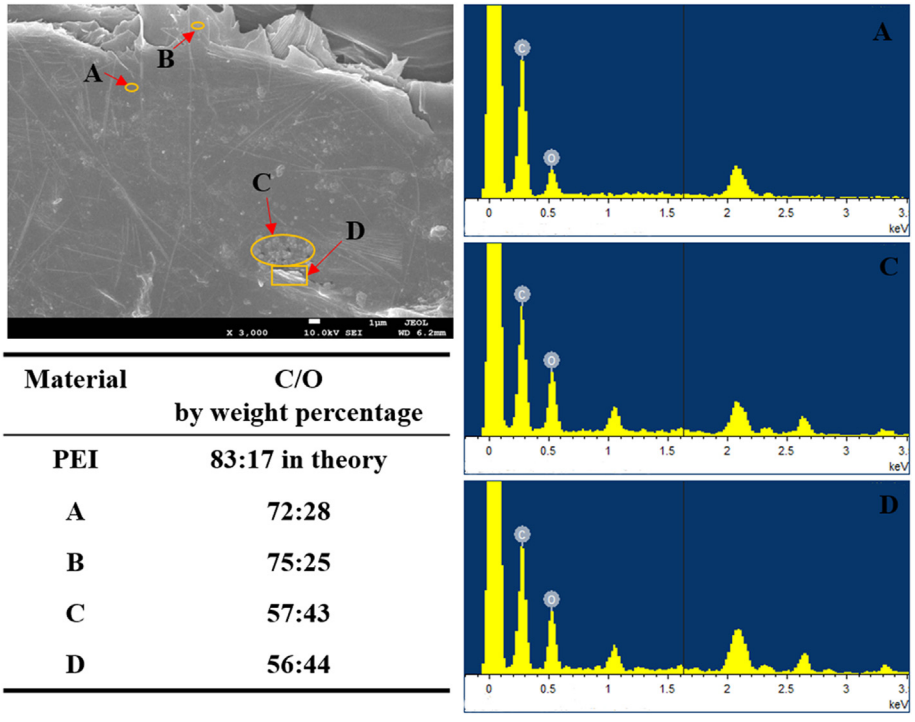


Fig. 3. Surface aspects of sizing films by SEM: (a) PEI + GO0, (b) PEI + GO1, (c) PEI + GO5, (d) PEI + GO10, (e) PEI + GO15.

3.2. Sizing film formulation

For sizing, the coating, and consequently the formation of a film, is very important. As shown in Fig. 1, the dispersions in bottles are basically yellow in appearance, from left to right, the contents of GO increase. The color of dispersions changes from light yellow to dark khaki, that is, the more GO exists, the darker it appears. All prepared dispersions are able to form perfect films after NMP evaporation. To further investigate the quality of films, their surface aspects are observed by SEM. As shown in Fig. 3. The surface aspects present more and more wrinkles and bulges with the increase of GO in PEI. The addition of GO can change the surface aspects of the films, thus affecting the interfacial microstructure of carbon fibers after sizing. However, excess addition will make GO agglomeration



Material	C/O by weight percentage
PEI	83:17 in theory
A	72:28
B	75:25
C	57:43
D	56:44

Fig. 4. Further EDS analysis of sizing film (PEI + GO15) at different positions.

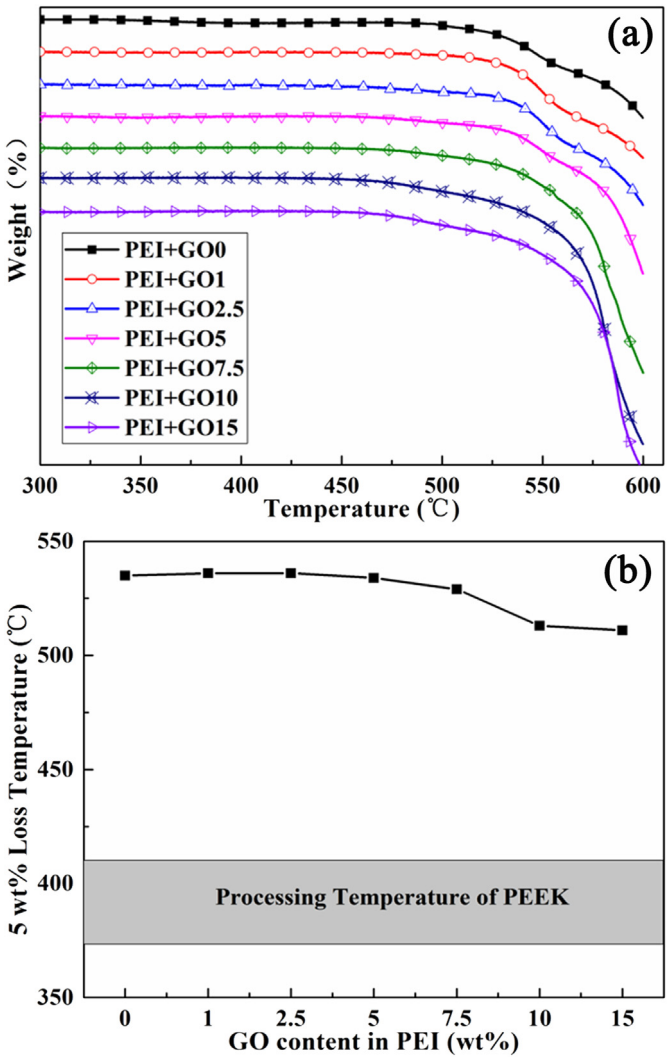


Fig. 5. Thermal stability analysis of PEI and GO complex films: (a) thermogravimetric curves in nitrogen, (b) 5 wt% loss temperatures.

easily, considering that the closely adjacent GO sheets are reduced and then reunited at the high processing temperature during the film formation [40–43] seen in the top right corner image of Fig. 3e (magnified image in Fig. 4).

In Fig. 4, energy dispersive spectrometer (EDS) analysis is adopted to investigate the composition of different regions [44]. The carbon and oxygen atom ratio of PEI is theoretically 83 to 17 by weight percentage. The flat regions (A and B) have similar carbon and oxygen atom ratio, which is close to theoretical ratio of PEI. However, the agglomerated region C and bulge region D have more low carbon and oxygen atom ratio, suggesting that the two regions have more GO introduced. In other words, it can be speculated that there exists more GO in the wrinkle or bulge regions in Fig. 3. SEM and EDS results prove that high contents of GO (15 wt% in PEI) can produce agglomeration, which may affect the interfacial performance of CF/PEEK composites after sizing.

The sizing agents are designed to increase the interfacial interactions and bonding of CF/PEEK composites or other high-temperature thermoplastic composites, so the thermal stability of PEI and GO complex films is a very important property at high processing temperature [45]. As shown in Fig. 5, they present high loss temperatures. The 5 wt% loss temperatures are more than 500 °C, which are far higher than the processing temperature of PEEK.

3.3. Surface morphologies of modified carbon fibers

The surface morphologies of carbon fibers are changed after sizing at different ratios of PEI and GO, as shown in Fig. 6. As for the surface morphologies of carbon fibers treated by the complex sizing with varied contents of GO, more wrinkles and bulges can be observed corresponding to the results of Fig. 3. The sizing thickness of modified carbon fibers is about 0.1–0.2 μm, which is obtained from SEM images.

Furthermore, detailed surface topography images are obtained by AFM to further analyze the effect of the sizing on the surfaces of carbon fibers, as shown in the upper right corner of Fig. 6. Some significant changes of carbon fiber surfaces are observed after the sizing treatment. Compared to bare fibers, the shallow grooves have been filled up for carbon fibers sized by PEI + GO0 seen in Fig. 6b. After the introduction of GO sheets, the randomly dispersed GO sheets can be identified in Fig. 6c-f. The results indicate that more GO sheets are presented on the fiber surfaces, thus increasing the surface roughness. In Fig. 6c, some uneven distribution of GO sheets on the surfaces can be observed. With the increase of GO contents from 1 wt% to 10 wt%, GO sheets can cover the entire carbon fiber surfaces homogeneously, as seen in Fig. 6d and e. However, some big bulges can be observed in Fig. 6f, mainly due to GO agglomeration during the film formation, corresponding to the phenomena in Figs. 3 and 4. The interface microstructure can affect the interfacial damping and the improvement of interfacial strength in CF/PEEK composites.

3.4. Micro-interfacial performance

Interfacial shear strength (IFSS) results of modified carbon fiber reinforced PEEK composites have been presented in Fig. 7, and the data are listed in Table A.1 (Appendix A). Based on the morphology analysis of the SEM and AFM images, it can be concluded that GO sheets surrounding the carbon fibers with the help of PEI contribute to the improvement of IFSS. It can be seen that the IFSS increases by 13.8% from 43.4 MPa for the bare carbon fibers to 49.5 MPa for the carbon fibers coated with PEI + GO0 sizing, which has been demonstrated a similar contribution in the literature shown in Table 1. More importantly, due to the introduction of GO, the IFSS increases by 40% and 44% for the carbon fibers coated with PEI + GO7.5 and PEI + GO10 sizing, respectively. The distinct enhancement effects of GO sheets are observed. Because excess addition of GO in sizing may agglomerate in the interfacial regions. It can bring about the local stress concentration [23,31] and increase the chances for crack initiation and propagation. It explains the reason that the IFSS only increase by about 25.3% for PEEK and carbon fibers coated with PEI + GO15 sizing.

Furthermore, the IFSS after hygrothermal treatment is also investigated for modified carbon fibers/PEEK composites, as shown in Fig. 7b. After hygrothermal treatment, an obvious decrease in IFSS by 10%-20% is observed for bare fibers from 43.4 MPa to 38.4 MPa and for fibers coated with PEI + GO10 sizing from 62.5 MPa to 53.2 MPa, respectively. Since water can act as a lubricant and plasticizer, when water diffuses into the interface, the interfacial debonding of CF/PEEK composites will occur [23,46]. However, the introduction of GO sheets can keep good mechanical interlocking, thus the IFSS for carbon fiber coated with complex sizing is still higher than that of bare fiber or carbon fibers only coated with PEI sizing after hygrothermal treatment. The mechanical interlocking of GO sheets can be confirmed by this and shows a positive effect on the interface of carbon fiber and PEEK.

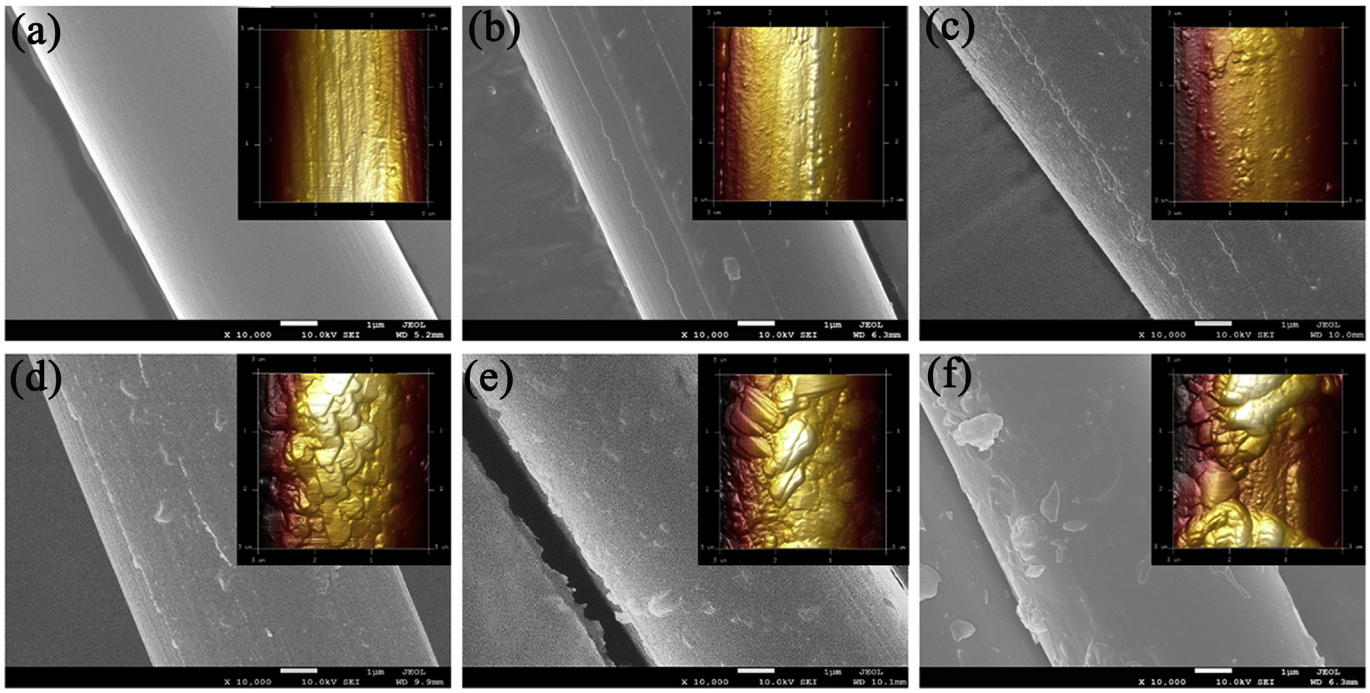


Fig. 6. SEM and AFM images of carbon fiber surfaces after sizing: (a) bare fiber without sizing, (b) PEI + GO0, (c) PEI + GO1, (d) PEI + GO5, (e) PEI + GO10, (f) PEI + GO15.

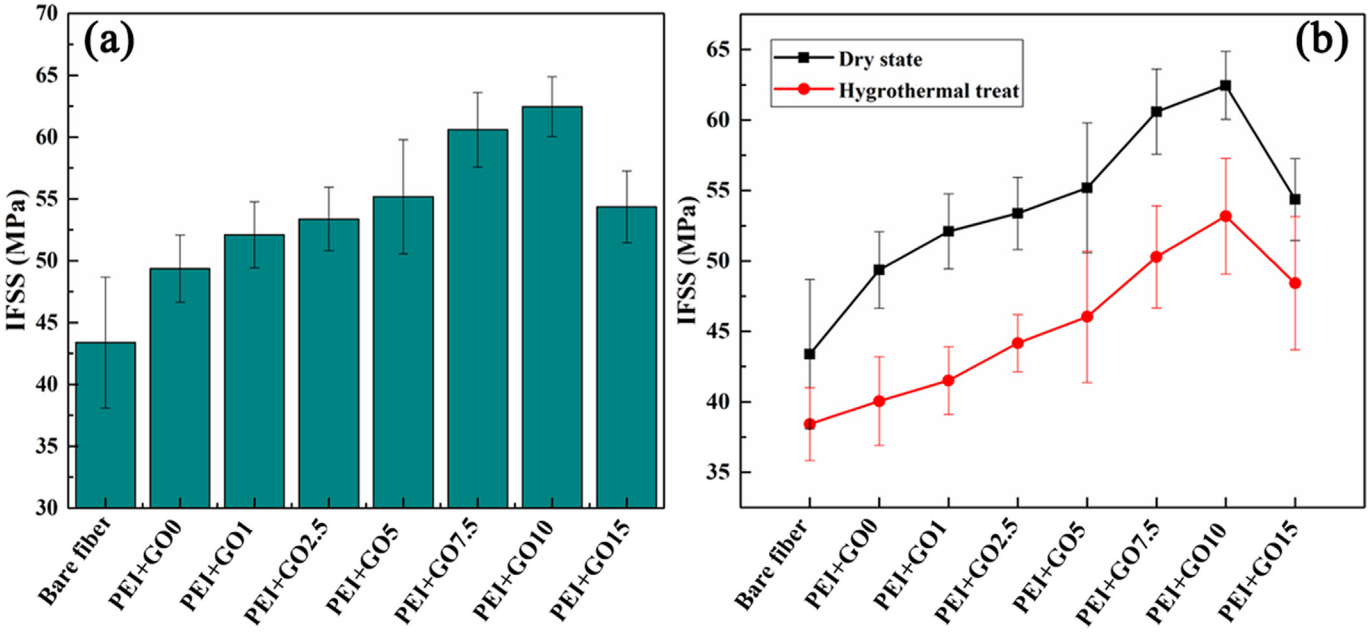


Fig. 7. Micro interfacial shear strength results of CF/PEEK composites with different carbon fiber treatments: (a) IFSS tested in dry state, (b) comparison of IFSS results tested in dry state and after hygrothermal treat.

Table 1
IFSS comparison of carbon fiber reinforced high-temperature thermoplastic composites in this study to others previous work.

Materials	Interface modification method	IFSS/MPa	References
CF(T700)/PEEK	Untreated—Sizing:PEI + GO/NMP	43.4—Max: 62.5	Our study
CF/PEEK	Untreated—Air oxidation—Ozone	35—47—56	[20]
CF(T700)/PPEK	Untreated—Sizing: PPEK/NMP	39.51—51.49	[21]
CF/PEEK	Untreated—Sizing: different polyimide	38—Max: 50	[22]
CF/PEEK	AS4 (high strength—HMS (high modulus)	38.9—24.7	[48]
CF/PES	Untreated—Sizing: polyamic acid	34—50	[23]
CF/PA6	Untreated—Ozone	35—56	[7]

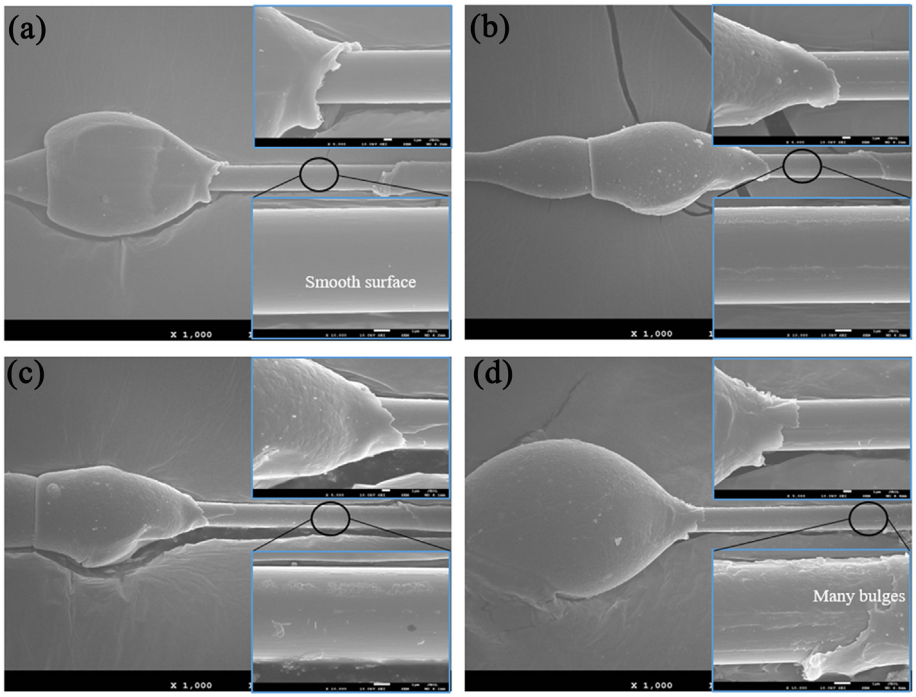


Fig. 8. SEM images of microbond test after debonding: (a) bare fiber without sizing, (b) PEI + GO0, (c) PEI + GO5, (d) PEI + GO10.

It is difficult to form stable chemical bonding by modifying carbon fibers directly due to the high processing temperature and inert feature of polymer. However, many other special surface treatment methods [7,20–23,47] are adopted to increase the interfacial bonding as shown in Table 1. In our study, the significant improvement in IFSS of CF/PEEK composites is mainly attributed to the PEI and GO complex sizing layer on the surfaces of carbon fibers. PEEK chains can diffuse into the sizing layer at high processing temperature and pressure (the sizing layer is very filmy). Actually, the complex interface layer may be made of PEI, PEEK and GO. The fully integrated interface region can effectively present the synergistic effects of sizing polymer and nano particles and enhance the interfacial interactions. As shown in Fig. 8, the failure morphologies of microbond test are observed by SEM. It can be seen in Fig. 8a that the debonding failure surfaces of bare carbon fiber and PEEK microdroplet present a smooth topography without any residual resin. A little resin remains on the failure surfaces of carbon fibers only coated with PEI in Fig. 8b. It is noted that with further adding GO in PEI sizing, the debonding failure surfaces are no longer smooth, and many bulges (resin and graphene) remain as seen in Fig. 8c and d. Obviously, the nano sheets are highly effective in increasing the mechanical interlocking and suppressing the crack propagation at the interface [48]. Based on the above analysis, the micro-bonding mechanism of modified carbon fibers and PEEK is illustrated in Fig. A.3 (Appendix A). It can be concluded that the five factors to affect the interfacial bonding of CF/PEEK composites are the miscible feature (PEEK and PEI), diffusion and entanglement (PEEK and PEI), mechanical interlocking (graphene and fiber, PEI and fiber, PEEK and fiber), adsorption (PEI and fiber, PEEK and fiber), and molecular interaction force (PEI and fiber, PEEK and fiber, PEI and graphene, PEEK and graphene, PEI and PEEK), respectively.

3.5. Dynamic mechanical behavior

The DMA test is employed to investigate the elastic stiffness and a damping (energy dissipation) term of CF/PEEK composites as a response to a low-strain periodic deformation. Typical results, including variation of storage modulus, G′, and tanδ as a function of temperature at 1 Hz are shown in Fig. 9. Keusch et al. [49] have revealed that the storage modulus is proportional and tanδ is inversely proportional to the interfacial bonding. It can be seen that the initial storage modulus increases for modified carbon fiber composites in Fig. 9a, suggesting improved interfacial bonding of carbon fibers and PEEK after fiber modification. However, we cannot further obtain the anticipated storage modulus changes of different modified fibers reinforced PEEK composites. Because the fiber-dominated dynamic properties (G′) is easy to be influenced by the slight change of fiber content in each small sample.

Since the damping term tanδ is a genuine indicator of all molecular motions in a given material, its estimation will enable us to quantify the interfacial bonding of modified carbon fibers and PEEK [50,51]. The glass transition temperatures, T_g (defined as the peak temperature of tanδ) for composites are listed in Table 2. It can be seen that all material systems exhibit similar glass transition temperatures, which does not change remarkably. However, damping at the glass transition temperature of bare fiber composites is much higher than that of modified carbon fiber composites. The difference can be attributed to the poor bonding. The tan δ_{max} at the temperature point T_g decrease by 3.1% from 4.775 for bare fiber composites to 4.628 for composites with PEI + GO0 sizing. The value of tan δ_{max} further decreases to 10%-20% due to the introduction of GO sheets. In a composite, the molecular motions at the interface contribute to the damping of the material. The strong interactions of carbon fibers and PEEK tend to decrease the damping tan δ_{max} and the area under the tan δ curve [50]. As shown in Table 2, compared to carbon fibers without coating, the normalized damping area results of carbon fibers coated with PEI + GO0, PEI + GO1, PEI + GO2.5, PEI + GO5, PEI + GO7.5, PEI + GO10 and PEI + GO15 decrease by 21%, 42%, 41%, 49%, 46%, 45%, and 36%, respectively. The introduction of PEI and GO complex sizing has more benefits in improving the interfacial bonding than only introducing PEI sizing. Furthermore, we can confirm that PEEK

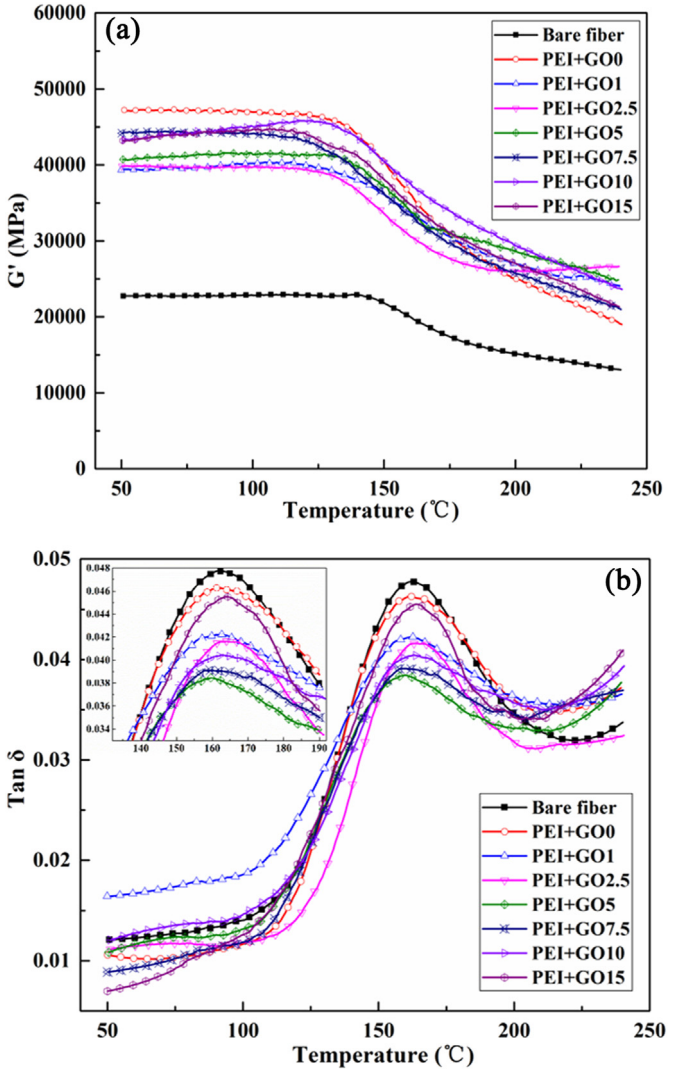


Fig. 9. Dynamic mechanical performance of macro CF/PEEK composites with different carbon fiber treatments: (a) the storage modulus, (b) the damping term.

Table 2
Detailed damping term tanδ analysis of CF/PEEK composites with different carbon fiber treatments.

Composites	T_g / °C	Tan $\delta_{max} \times 10^{-2}$	Normalized area of Tan δ	β
Bare fiber	161	4.775	100	1.516
PEI + GO0	161	4.628	79	1.531
PEI + GO1	163	4.223	58	1.572
PEI + GO2.5	164	4.164	59	1.578
PEI + GO5	160	3.845	51	1.611
PEI + GO7.5	160	3.911	54	1.604
PEI + GO10	163	4.044	55	1.590
PEI + GO15	164	4.550	64	1.539

reinforced by carbon fibers coated with PEI + GO5, PEI + GO7.5, and PEI + GO10 sizing show strong interfacial bonding in the whole damping process (about from 100 °C to 220 °C).

It is assumed that at ambient temperature the damping of carbon fibers is negligible and energy dissipation in CF/PEEK composites is attributed to the matrix PEEK and fiber/matrix interactions at the interface regions, thus the interfacial strength indicator β has been given by Sarasua et al. [52].

$$\beta = \left(1 - \frac{\tan\delta_c}{\tan\delta_m}\right) \Big/ V_f \tag{2}$$

where tan δ_c and tan δ_m refer to the tan δ_{max} of composites and matrix in the damping process (the glass transition), respectively, and V_f is the fiber volume fraction. Input data are obtained by actual determination, V_f = 50% and tan δ_m = 0.197 (see the Fig. A.4 in Appendix A). The results are listed in Table 2. The stronger the interfacial interactions are, the higher the value of parameter β will be. It can be observed that under the dynamic loading, PEEK reinforced by carbon fibers coated with PEI and GO complex sizing (GO addition 5-10 wt%) still show good interfacial bonding, confirming the excellent synergistic effects at the interface.

3.6. Interlaminar shear performance

Interlaminar shear strength (ILSS) test has been employed to evaluate the interfacial bonding of macro composites. The ILSS will further demonstrate the effects of PEI and GO complex sizing on

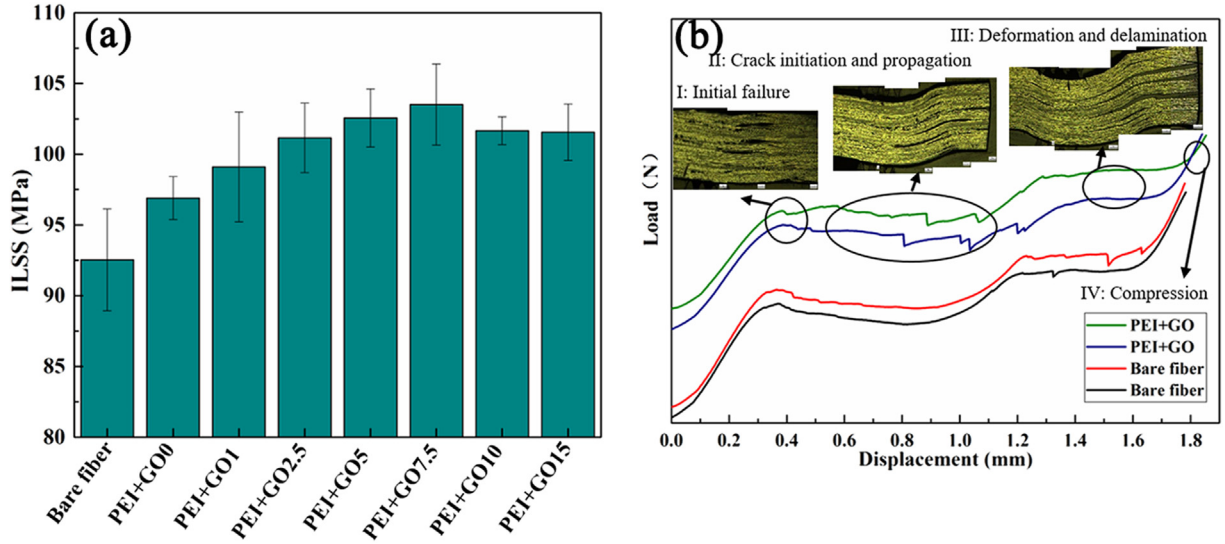


Fig. 10. Interlaminar shear strength results: (a) the ILSS data of CF/PEEK composite with different carbon fiber treatments, (b) further analysis about interlaminar shear testing curves before and after sizing.

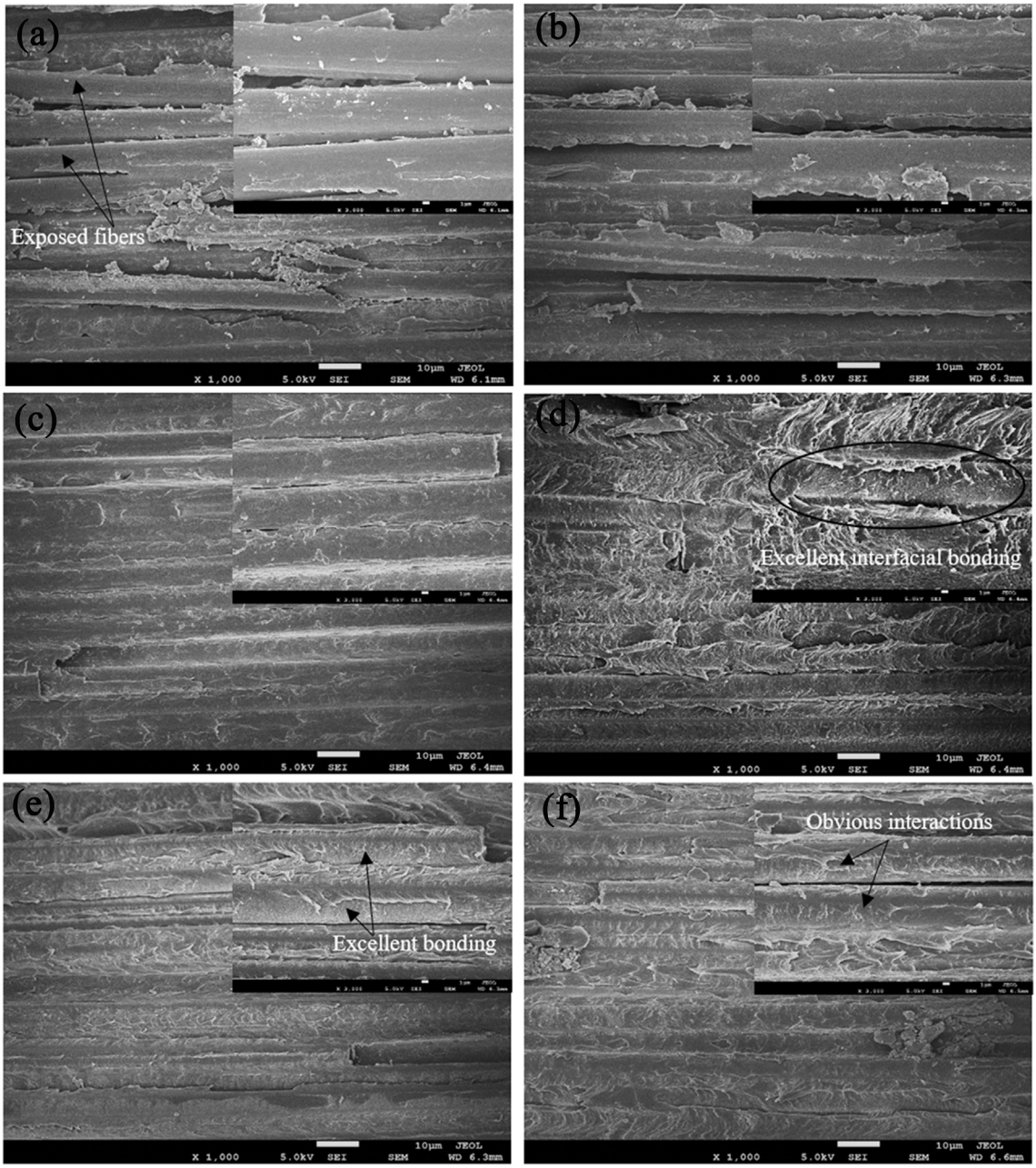


Fig. 11. SEM images of CF/PEEK composites with different carbon fiber treatments after ILSS fracture: (a) bare fiber without sizing, (b) PEI + GO0, (c) PEI + GO1, (d) PEI + GO5, (e) PEI + GO10 (f) PEI + GO15.

interfacial interactions in CF/PEEK composites. As shown in Fig. 10a, the ILSS of CF/PEEK composites increases by 12% from 92.5 MPa for bare carbon fibers without sizing to 103.5 MPa (a maximum ILSS) for carbon fibers with PEI + GO7.5 sizing. Compared to carbon fibers only sized by PEI, the introduction of GO sheets makes greater contribution on ILSS. It can be concluded that the homogenously dispersed GO sheets surrounding carbon fiber surfaces can greatly increase the interfacial bonding [53–55], as revealed by IFSS and DMA results.The maximum ILSS is obtained in GO loading from 5 to 7.5 wt%. Excessive addition of nano sheets will influence the transfer of interfacial stress [56,57]. For macro composites, more or less deviation of manufacturing and testing of different specimen will exist. Based on above informations, a suitable addition of GO in PEI about 5–10 wt% is obtained.

The typical interlaminar shear testing curves are observed, which reveal a different damage mechanism from that of thermoset composites [58]. There does not exist a sudden break of ILSS specimen, as shown in Fig. 10b, which means that the disaster failure does not take place due to the excellent toughness of PEEK [59]. Besides, four typical failure stages of ILSS testing can be seen for CF/PEEK composites. For the first stage, the initial failure is produced with the increase of load. For the second stage, more and more cracks are further induced, and then propagate along the interface. A slight decrease of load is observed in this stage. The maximum stress in the first and second stage is defined as the ILSS. The third stage can no longer reveal the interlaminar or interfacial failure due to the distinct deformation and delamination. For the last stage, the specimen will be further compressed until broken

under the pressure. Obviously, due to the introduction of PEI and GO complex sizing on carbon fiber surfaces, the fluctuant curves in the second stage can be observed with higher load than the initial failure load sometimes. However, for bare fiber without sizing, their ILSS curves present a smooth state in the second stage, showing lower load. It means that in the course of crack initiation and propagation, the PEI and GO complex sizing layer can increase interfacial bonding effectively [60], and act as a barrier for crack propagation, thus this course can increase the fracture energy and lead to the fluctuation of Load-Displacement curves.

In order to understand the interfacial behavior and interaction mechanism of modified carbon fiber reinforced PEEK composites, the fracture surfaces of ILSS specimen is investigated as shown in Fig. 11. Some smooth surfaces of carbon fibers can be observed due to the poor bonding in Fig. 11a. Although some PEEK resin still remains on the fiber, their interactions at the interface are clearly weak. With the addition of PEI on carbon fibers in Fig. 11b, more resin can be seen adhering to carbon fiber surfaces after fracture, which still shows weak interactions. The same phenomena can be also found in Fig. 11c, even despite a small amount of GO sheets introduced into the interface regions. It indicates that more addition of GO sheets into PEI for sizing is necessary. Obviously, the different interface microstructure is observed in Fig. 11c and d mainly due to the increasing introduction of GO sheets. The jagged surface morphologies are further investigated, indicating that the strong interactions take place at the interface [61]. PEEK chain can diffuse into the sizing layer at high processing temperature and pressure. Actually, the complex interface layer may be made of PEI, PEEK and GO. When the cracks are induced under the shearing load, these stiff and tough sheets can block the initial cracks, reducing the stress intensity factors at the crack tips [62], thus the local intensive energy is absorbed. On the other hand, increasing the barrier for cracks propagation in the ongoing direction can make these cracks change the propagation direction, increasing the energy dissipation [63], so the jagged morphologies can be seen. Some of these estimations have been approved by AFM images, IFSS and DMA test results as mentioned above. Further, as shown in Fig. 12, the interfacial interactions and crack propagation between fibers and PEEK matrix have been illustrated.

3.7. Flexural performance

In order to further investigate the comprehensive effects of PEI and GO complex sizing on CF/PEEK composites, the flexural behaviors are evaluated, which actually reflect the structural characteristics of the modified laminates in response to complex stress states (bending stress and shearing stress) [64]. The results of flexural tests are shown in Fig. 13. It can be observed that the flexural strength of modified carbon fiber reinforced PEEK composites is higher than that of the bare fiber composites without any modification. With the increase of GO contents (about 5–10 wt%), the flexural strength grows up to about 1730 MPa. A slight decrease in flexural strength is seen when the GO content increases to 15 wt % in sizing. As for flexural modulus in Fig. 13, there are small fluctuation around 110 GPa without increasing greatly, but a slight increase of flexural modulus by 5% can be achieved by the addition of 2.5–7.5 wt% GO in PEI as the sizing in comparison with that of bare fiber reinforced composites. Generally, this slight change in modulus can be engineering errors and be also ignored in the actual production. But the increase of flexural strength is remarkable. However, excess addition of GO sheets in sizing is not beneficial to forming the homogeneous interface, and impeding further enhancement of flexural performance. The results demonstrate that the flexural performance of composites can be improved by optimizing the interface composition [65]. It can be concluded that

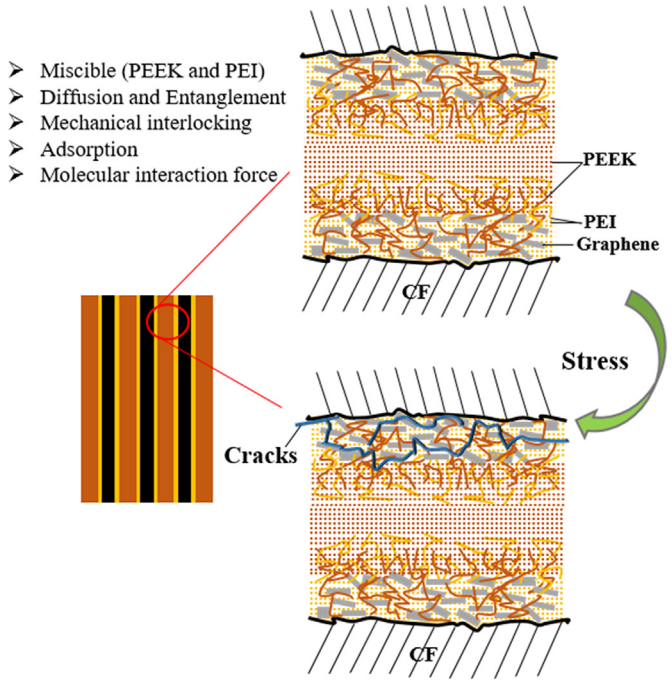


Fig. 12. Schematic illustration of bonding mechanism in macro CF/PEEK composites before and after failure.

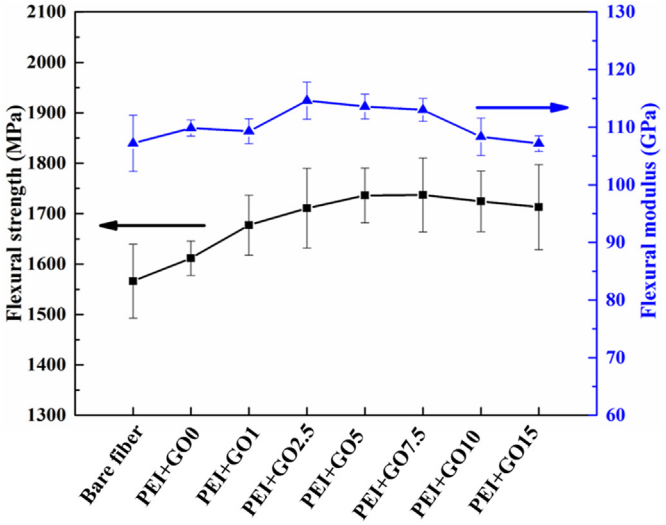


Fig. 13. Flexural performance results of CF/PEEK composites with different carbon fiber treatments.

the strong interfacial interaction and bonding can increase the resistance to failure.

To better understand the enhancing mechanism of introducing GO and PEI complex sizing at the interface of CF/PEEK composites, the lower surfaces of specimen subjected to the tensile load in the flexural test are presented in Fig. 14. For bare fiber reinforced PEEK composites, their fracture morphologies reveal the interfacial debonding and fiber pullout [66]. The flat fracture surfaces can be also observed in Fig. 14a, which reflects the poor load transfer between fiber and matrix. In contrast, after the introduction of PEI and GO complex sizing, the excellent adhesion at the interface of CF/

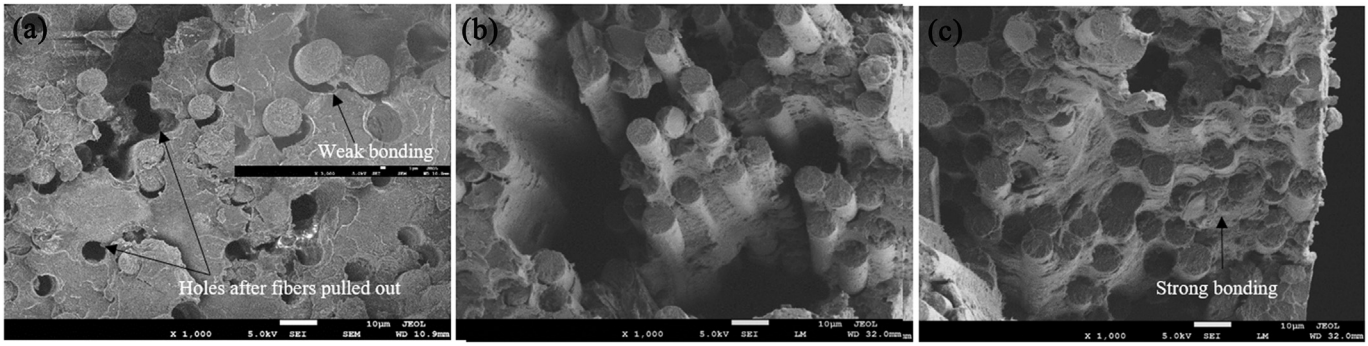


Fig. 14. SEM images of flexural test of CF/PEEK composites with different carbon fiber treatments after fracture: (a) bare fiber without sizing, (b) PEI + GO1, (c) PEI + GO10.

PEEK composites can be observed. With further increase in GO contents, the failure modes change, as seen in Fig. 14b and c. This phenomenon is probably attributed to the fact that a suitable addition of GO sheets in sizing can achieve tight adhesion and strong interfacial interactions, enhancing the load transfer, as shown in Fig. 12. Besides, the same as ILSS, further increasing GO contents in the sizing will cause local stress concentration due to GO agglomeration in the interfacial region.

4. Conclusions

In summary, an effective method to increase the interface interactions and bonding of CF/PEEK composites by introducing PEI and GO complex sizing to the CF surfaces is presented, showing potential application in improving interfacial performance during the manufacture of fiber reinforced high-temperature thermoplastic prepregs or composites in production line. It is observed that sizing layer forms on the fiber homogeneously and GO sheets are introduced successfully on carbon fiber surfaces after sizing. The IFSS increases by 44% from 43.4 MPa to 62.5 MPa for the carbon fibers coated with PEI + GO10 sizing. After hygrothermal treatment, the existence of GO sheets can keep good mechanical interlocking between carbon fibers and PEEK, thus the IFSS for carbon fibers coated with PEI and GO complex sizing are still higher than that of bare fibers or carbon fibers only coated with PEI sizing.

Furthermore, compared to the bare carbon fibers, the normalized damping area results of carbon fibers coated with PEI and GO complex sizing decrease remarkably (maximum reduction about 50%), suggesting better interfacial bonding. DMA results also show that the introduction of PEI and GO complex sizing has more benefits than only introducing PEI sizing. The interfacial strength indicator calculated from the peak data of damping term shows good agreement with damping areas. The ILSS value of CF/PEEK composites increases by 12% from 92.5 MPa to 103.5 MPa. DMA results, ILSS test and flexural test results are in agreement with each other, suggesting better interface bonding of composites by applying PEI and GO complex sizing. Finally, the interfacial interaction mechanisms are proposed. Improving the interfacial miscibility and mechanical interlocking proves to be a strategy to increase the interfacial interactions and bonding in high-temperature thermoplastic composites.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.compscitech.2017.11.005.

References

[1] K.J. Wong, U. Nirmal, B.K. Lim, Impact behavior of short and continuous fiber-reinforced polyester composites, J. Reinf. Plast. Compos 29 (2010) 3463–3474.
[2] B. Vieille, V.M. Casado, C. Bouvet, About the impact behavior of woven-ply carbon fiber-reinforced thermoplastic-and thermosetting-composites: a comparative study, Compos. Struct. 101 (2013) 9–21.
[3] M.H. Akonda, C.A. Lawrence, B.M. Weager, Recycled carbon fibre-reinforced polypropylene thermoplastic composites, Compos. Part A 43 (1) (2012) 79–86.
[4] J. Markarian, Processing and recycling advantages drive growth in thermoplastic elastomers, Plast. Addit. Compd. 6 (2004) 22–25.
[5] H. Guo, Y. Huang, L. Liu, X. Shi, Effect of epoxy coatings on carbon fibers during manufacture of carbon fiber reinforced resin matrix composites, Mater. Des. 31 (2010) 1186–1190.
[6] R. Sa, Y. Yan, Z. Wei, L. Zhang, W. Wang, M. Tian, Surface modification of aramid fibers by bio-inspired poly (dopamine) and epoxy functionalized silane grafting, ACS Appl. Mater. Interfaces 6 (2014) 21730–21738.
[7] J. Li, Interfacial studies on the O_3 modified carbon fiber-reinforced polyamide 6 composites, Appl. Surf. Sci. 255 (2008) 2822–2824.
[8] A.L. Santos, E.C. Botelho, K.G. Kostov, M. Ueda, L.L.G. Da Silva, Carbon fiber surface modification by plasma treatment for interface adhesion improvements of aerospace composites, Adv. Mater. Res. 1135 (2016) 75.
[9] H.S. Lee, S. Kim, Y.J. Noh, S.Y. Kim, Design of microwave plasma and enhanced mechanical properties of thermoplastic composites reinforced with microwave plasma-treated carbon fiber fabric, Compos. Part B 60 (2014) 621–626.
[10] N. Li, L. Zong, Z. Wu, C. Liu, J. Wang, X. Jian, Effect of Poly (phthalazinone ether ketone) with amino groups on the interfacial performance of carbon fibers reinforced PPBES resin, Compos. Sci. Technol. 149 (2017) 178–184.
[11] L. Sorrentino, G. Simeoli, S. Iannace, P. Russo, Mechanical performance optimization through interface strength gradation in PP/glass fibre reinforced composites, Compos. Part B 76 (2015) 201–208.
[12] A. El-Sabbagh, Effect of coupling agent on natural fibre in natural fibre/polypropylene composites on mechanical and thermal behaviour, Compos. Part B 57 (2014) 126–135.
[13] D.T. Burn, L. Harper, M. Johnson, N.A. Warrior, L. Yang, J. Thomason, The influence of coupling agent, fibre sizing and matrix degradation on the interfacial shear strength between carbon fibre and polypropylene, in: 16th European Conference on Composite Materials, 2014.
[14] Y. Ming, L. Yao, L. Qiujun, Y. Di, The interlaminar shear strength and tribological properties of PA 6 composites filled with graphene oxide-treated carbon fiber, Surf. Interface Anal. 49 (2017) 755–758.
[15] M. Mudhukrishnan, P. Hariharan, K. Palanikumar, B. Latha, Tool materials influence on surface roughness and oversize in machining glass fiber reinforced polypropylene (GFR-PP) composites, Mater. Manuf. Process (2016) 1–10.
[16] M. Haddad, R. Zitoune, F. Eyma, B. Castanié, Influence of machining process and machining induced surface roughness on mechanical properties of continuous fiber composites, Exp. Mech. 55 (2015) 519–528.
[17] A.M. Díez-Pascual, M. Naffakh, C. Marco, M.A. Gómez-Fatou, G.J. Ellis, Multiscale fiber-reinforced thermoplastic composites incorporating carbon nanotubes: A review, Solid State Mater. Sci. 18 (2014) 62–80.
[18] I. Giraud, S. Franceschi-Messant, E. Perez, C. Lacabanne, E. Dantras, Preparation of aqueous dispersion of thermoplastic sizing agent for carbon fiber by emulsion/solvent evaporation, Appl. Surf. Sci. 266 (2013) 94–99.
[19] J. Duchoslav, C. Unterweger, R. Steinberger, C. Fürst, D. Stifter, Investigation on the thermo-oxidative stability of carbon fiber sizings for application in

thermoplastic composites, Polym. Degrad. Stabil. 125 (2016) 33–42.
[20] J. Li, Interfacial studies on the ozone and air-oxidation-modified carbon fiber reinforced PEEK composites, Surf. Interface Anal. 41 (2009) 310–315.
[21] L. WenBo, Z. Shu, H. LiFeng, J. WeiCheng, Y. Fan, L. XiaoFei, W. RongGuo, Interfacial shear strength in carbon fiber-reinforced poly (phthalazinone ether ketone) composites, Polym. Compos 34 (2013) 1921–1926.
[22] S.L. Chuang, N.J. Chu, W.T. Whang, Effect of polyamic acids on interfacial shear strength in carbon fiber/aromatic thermoplastics, J. Appl. Polym. Sci. 41 (1990) 373–382.
[23] H. Yuan, S. Zhang, C. Lu, S. He, F. An, Improved interfacial adhesion in carbon fiber/polyether sulfone composites through an organic solvent-free polyamic acid sizing, Appl. Surf. Sci. 279 (2013) 279–284.
[24] N. Li, Z. Wu, L. Huo, L. Zong, Y. Guo, J. Wang, X. Jian, One-step functionalization of carbon fiber using in situ generated aromatic diazonium salts to enhance adhesion with PPBES resins, RSC Adv. 6 (2016) 70704–70714.
[25] N. Li, L. Zong, Z. Wu, C. Liu, X. Wang, F. Bao, J. Wang, X. Jian, Amino-terminated nitrogen-rich layer to improve the interlaminar shear strength between carbon fiber and a thermoplastic matrix, Compos. Part A 101 (2017) 490–499.
[26] Heon Sang Lee, Woo Nyon Kim, Glass transition temperatures and rigid amorphous fraction of poly(ether ether ketone) and poly(ether imide) blends, Polymer 38 (11) (1997) 2657–2663.
[27] Jong Hyun Yoo, N.S. Eiss, Tribological behavior of blends of polyether ether ketone and polyether imide, Wear 162 (1993) 418–425.
[28] I. Giraud, S. Franceschi, E. Perez, C. Lacabanne, E. Dantras, Influence of new thermoplastic sizing agents on the mechanical behavior of poly (ether ketone ketone)/carbon fiber composites, J. Appl. Polym. Sci. 132 (2015).
[29] B.A. Patterson, H.A. Sodano, Enhanced Interfacial Strength and UV Shielding of Aramid Fiber Composites through ZnO Nanoparticle Sizing, ACS Appl. Mater. Interfaces 8 (2016) 33963–33971.
[30] B. Yu, Z. Jiang, X. Tang, C.Y. Yue, J. Yang, Enhanced interphase between epoxy matrix and carbon fiber with carbon nanotube-modified silane coating, Compos. Sci. Technol. 99 (2014) 131–140.
[31] X. Zhang, X. Fan, C. Yan, H. Li, Y. Zhu, X. Li, L. Yu, Interfacial microstructure and properties of carbon fiber composites modified with graphene oxide, ACS Appl. Mater. Interfaces 4 (2012) 1543–1552.
[32] J. George, M.S. Sreekala, S. Thomas, A review on interface modification and characterization of natural fiber reinforced plastic composites, Polym. Eng. Sci. 41 (2001) 1471–1485.
[33] S. Zhandarov, E. Mäder, Characterization of fiber/matrix interface strength: applicability of different tests, approaches and parameters, Compos. Sci. Technol. 65 (2005) 149–160.
[34] L. Yang, J.L. Thomason, Interface strength in glass fibre–polypropylene measured using the fibre pull-out and microbond methods, Compos. Part A 41 (2010) 1077–1083.
[35] B. Liu, Z. Liu, X. Wang, G. Zhang, S. Long, J. Yang, Interfacial shear strength of carbon fiber reinforced polyphenylene sulfide measured by the microbond test, Polym. Test. 32 (2013) 724–730.
[36] B. Yu, Z. Jiang, J. Yang, Long-term moisture effects on the interfacial shear strength between surface treated carbon fiber and epoxy matrix, Compos. Part A 8 (2015) 311–317.
[37] Y. Wang, Y. Zhao, T. Bao, X. Li, Y. Su, Y. Duan, Preparation of Ni-reduced graphene oxide nanocomposites by Pd-activated electroless deposition and their magnetic properties, Appl. Surf. Sci. 258 (2012) 8603–8608.
[38] M. Liu, Y. Duan, Y. Wang, Y. Zhao, Diazonium functionalization of graphene nanosheets and impact response of aniline modified graphene/bismaleimide nanocomposites, Mater. Des. 53 (2014) 466–474.
[39] G. Yang, G. Zhang, P. Sheng, F. Sun, W. Xu, D. Zhang, A new approach to reduced graphite oxide with tetrathiafulvalene in the presence of metal ions, J. Mater. Chem. 22 (2012) 4391–4395.
[40] S. Stankovich, D.A. Dikin, R.D. Piner, K.A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S.T. Nguyen, R.S. Ruoff, Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide, Carbon 45 (2007) 1558–1565.
[41] W. Chen, L. Yan, P.R. Bangal, Preparation of graphene by the rapid and mild thermal reduction of graphene oxide induced by microwaves, Carbon 48 (2010) 1146–1152.
[42] Y. Zhang, W. Fan, Y. Huang, C. Zhang, T. Liu, Graphene/carbon aerogels derived from graphene crosslinked polyimide as electrode materials for supercapacitors, RSC Adv. 5 (2015) 1301–1308.
[43] S. Park, J. An, I. Jung, R.D. Piner, S.J. An, X. Li, A. Velamakanni, R.S. Ruoff, Colloidal Suspensions of Highly Reduced Graphene Oxide in a Wide Variety of Organic Solvents, Nano Lett. 9 (2009) 1593–1597.
[44] N. Zheng, Y. Huang, W. Sun, X. Du, H. Liu, S. Moody, J. Gao, Y. Mai, In-situ pull-off of ZnO nanowire from carbon fiber and improvement of interlaminar toughness of hierarchical ZnO nanowire/carbon fiber hydrid composite laminates, Carbon 110 (2016) 69–78.
[45] S. Kumar, T. Rath, R.N. Mahaling, C.S. Reddy, C.K. Das, K.N. Pandey, R.B. Srivastava, S.B. Yadaw, Study on mechanical, morphological and electrical properties of carbon nanofiber/polyetherimide composites, Mater. Sci. Eng. B 141 (2007) 61–70.
[46] J. Park, D. Kim, J. Kong, M. Kim, W. Kim, I. Park, Interfacial adhesion and microfailure modes of electrodeposited carbon fiber/epoxy–PEI composites by microdroplet and surface wettability tests, J. Colloid Interf. Sci. 249 (2002) 62–77.
[47] A. Lustiger, Morphological aspects of the interface in the PEEK-carbon fiber system, Polym. Compos 13 (1992) 408–412.
[48] R. Rafiq, D. Cai, J. Jin, M. Song, Increasing the toughness of nylon 12 by the incorporation of functionalized graphene, Carbon 48 (2010) 4309–4314.
[49] S. Keusch, R. Haessler, Influence of surface treatment of glass fibres on the dynamic mechanical properties of epoxy resin composites, Compos. Part A 30 (1999) 997–1002.
[50] A. Afaghi-Khatibi, Y. Mai, Characterisation of fibre/matrix interfacial degradation under cyclic fatigue loading using dynamic mechanical analysis, Compos. Part A 33 (2002) 1585–1592.
[51] S. Dong, R. Gauvin, Application of dynamic mechanical analysis for the study of the interfacial region in carbon fiber/epoxy composite materials, Polym. Compos 14 (1993) 414–420.
[52] J.R. Sarasua, J. Pouyet, Dynamic mechanical behavior and interphase adhesion of thermoplastic (PEEK, PES) short fiber composites, J. Thermoplast. Compos 11 (1998) 2–21.
[53] C.Y. Lee, J. Bae, T. Kim, S. Chang, S.Y. Kim, Using silane-functionalized graphene oxides for enhancing the interfacial bonding strength of carbon/epoxy composites, Compos. Part A 75 (2015) 11–17.
[54] W. Liao, H. Tien, S. Hsiao, S. Li, Y. Wang, Y. Huang, S. Yang, C.M. Ma, Y. Wu, Effects of Multiwalled Carbon Nanotubes Functionalization on the Morphology and Mechanical and Thermal Properties of Carbon Fiber/Vinyl Ester Composites, ACS Appl. Mater. Interfaces 5 (2013) 3975–3982.
[55] W. Lee, J.U. Lee, H. Cha, J. Byun, Partially reduced graphene oxide as a multifunctional sizing agent for carbon fiber composites by electrophoretic deposition, RSC Adv. 3 (2013) 25609–25613.
[56] H.A.J.A. Kuang-Ting, Use of epoxy/multiwalled carbon nanotubes as adhesives to join graphite fibre reinforced polymer composites, Nanotechnology 14 (2003) 791.
[57] J. Zhu, A. Imam, R. Crane, K. Lozano, V.N. Khabashesku, E.V. Barrera, Processing a glass fiber reinforced vinyl ester composite with nanotube enhancement of interlaminar shear strength, Compos. Sci. Technol. 67 (2007) 1509–1517.
[58] A. Agirregomezkorta, J. Zurbitu, G. Aretxaga, M. Sarrionandia, J. Aurrekoetxea, Strain rate effect on interlaminar shear strength of carbon fibre reinforced pCBT and epoxy composites, in: 17th International Conference of Composites Materials, ICCM17, 2009.
[59] L.B. Nohara, M.L. Costa, M.A. Alves, M.F.K. Takahashi, E.L. Nohara, M.C. Rezende, Processing of high performance composites based on peek by aqueous suspension prepregging, Mater. Res. 13 (2010) 245–252.
[60] X. Kong, F. Teng, H. Tang, L. Dong, Z. Feng, Miscibility and crystallization behaviour of poly (ether ether ketone)/polyimide blends, Polymer 37 (1996) 1751–1755.
[61] C. Marieta, E. Schulz, L. Irusta, N. Gabilondo, A. Tercjak, I. Mondragon, Evaluation of fiber surface treatment and toughening of thermoset matrix on the interfacial behaviour of carbon fiber-reinforced cyanate matrix composites, Compos. Sci. Technol. 65 (2005) 2189–2197.
[62] I. De Baere, S. Jacques, W. Van Paepegem, J. Degrieck, Study of the Mode I and Mode II interlaminar behaviour of a carbon fabric reinforced thermoplastic, Polym. Test. 31 (2012) 322–332.
[63] P.H. Thornton, Energy absorption in composite structures, J. Compos. Mater 13 (1979) 247–262.
[64] M.Z. Rong, M.Q. Zhang, Y. Liu, G.C. Yang, H.M. Zeng, The effect of fiber treatment on the mechanical properties of unidirectional sisal-reinforced epoxy composites, Compos. Sci. Technol. 61 (2001) 1437–1447.
[65] B.F. Yousif, A. Shalwan, C.W. Chin, K.C. Ming, Flexural properties of treated and untreated kenaf/epoxy composites, Mater. Des. 40 (2012) 378–385.
[66] H. He, J. Wang, K. Li, J. Wang, J. Gu, Mixed resin and carbon fibres surface treatment for preparation of carbon fibres composites with good interfacial bonding strength, Mater. Des. 31 (2010) 4631–4637.