

Research Article

Synergistically Improving Mechanical and Interfacial Properties of Epoxy Resin and CFRP Composites by Introducing Graphene Oxide

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In this study, graphene oxide (GO) was employed as nanoscale reinforcement for the development of high-performance carbon fiber reinforced plastic (CFRP) composites. Initially, epoxy resin was modified by incorporating GO with different weight proportion from 0.05 to 0.6 wt.%. Then the unidirectional CFRP composites were prepared with the modified epoxy resin by winding and compression molding technique. The optimized GO-CFRP composites with GO content of 0.1 wt.% present tensile strength of 2756 MPa and monofilament interfacial shear strength of 29.06 MPa, respectively, which are 14.4% and 12.5% higher than the corresponding values of the pristine CFRP composites. To intuitively observe the fracture process of the CFRP composites, the digital image correlation system was employed. It is verified that the moderate addition of GO can improve the stress concentration of the CFRP composites during the deformation process. In addition, the reinforcing mechanism is investigated by analyzing the fracture surface of the modified epoxy resin and the CFRP composites. The results indicate that GO can make the cracks deflect or bifurcate along with the epoxy resin which closes to graphene, resulting in synergistically improved mechanical and interfacial properties of the GO-modified CFRP composites.

1. Introduction

Fiber reinforced epoxy resin composites, such as carbon fiber [1, 2], natural fiber [3–5], and glass fiber [6, 7] composite materials, have been extensively employed in a wide range of applications such as aerospace, sports sector, civil construction, and automotive fields due to their superior strength to weight, high thermal stability, excellent structural design, and corrosion resistance. However, in the case of carbon fiber reinforced composites, the surface properties of carbon fibers such as smoothness, surface inertness, and poor wettability make their incorporation into an epoxy matrix difficult and result in poor interfacial adhesion [8, 9]. Meanwhile, because of the brittle texture, the cured epoxy resin is hard to suppress the generation and expansion of microcracks, resulting in poor impact resistance [10, 11].

All of the above drawbacks significantly limit the improvement of the mechanical and interfacial performance of carbon fiber-reinforced plastic (CFRP) composites. Consequently, the enhancement and toughening of the epoxy resin and the CFRP composites have attracted much attention [12–16]. Various materials such as rubber, block copolymers, thermoplastic resin, and other miscellaneous fillers have been adopted for toughening epoxy matrix and improving interfacial adhesion of CFRP composites [17–21].

Graphene, a typical two-dimensional carbon nanostructured material, has attracted wide attention due to the advantages of high electrical and thermal conductivity, high strength, high hardness, low thermal expansion coefficient, and large specific surface area [22]. However, graphene is rarely employed for improving the interfacial adhesion of CFRP composites because of the characteristics of

aggregation tendency, inert surface, and poor processability [23]. Instead, its oxide, Graphene oxide (GO) is a superior choice. The surface of GO contains a large number of oxygen-containing functional groups such as carboxyl, carbonyl, hydroxyl, and epoxy groups [24]. It can enhance the interaction between GO and the resin matrix and effectively improve the mechanical strength and toughness of the resin matrix [25, 26]. For example, Haddadi et al. [27] developed reduced graphene oxide nanoplate/epoxy composites by a cerium-doped tannic acid treatment method, where the mechanical properties were proved to be improved effectively. Moreover, GO also has a significant strengthening and toughening effect on carbon fiber-reinforced epoxy resin composites [23, 28, 29]. Watson et al. [30] prepared GO-modified CFRP composites by vacuum assisted resin infusion process, and found that the flexural strength and modulus of CFRP composites with 0.5 wt.% GO content increased by about 10% compared with those of unmodified composites. Zhang et al. [31] employed amino-rich GO nanosheets to modify epoxy resin and fabricate multiscale carbon fibers. The as-prepared CFRP composites exhibited superior interlaminar behavior.

From the published research, it can be verified that GO has an obvious strengthening and toughening effect on epoxy resin and CFRP composites. However, GO still readily aggregates under relatively high loading [32]. Several strategies can overcome this problem, such as the modification and reduction of GO by using organic compounds [27]. Silane modification of GO is a promising method for improving the properties of the composites among different modification methods [33, 34]. The alkoxy groups of the silane coupling agent can react with the hydroxyl groups of GO and the remained functional groups of silane molecules on GO sheets can produce a chemical bridge between GO and the epoxy resin matrix [33, 34].

In this regard, Li et al. [35] studied the mechanical properties of silane-functionalized GO-epoxy nanocomposites. Two differently terminated silane coupling agents including 3-aminopropyltriethoxy silane (APTES) and 3-glycidoxypropyltrimethoxy silane (GPTMS) were used. Wan et al. [33] used GPTMS to functionalize GO and their results showed that the storage modulus, glass transition temperature, thermal stability, tensile and flexural properties, and fracture toughness of epoxy composites were promoted. However, the preparation process of silane-functionalized GO was a little cumbersome. To simplify the fabrication process of the CFRP composites, our present work employs a convenient and operational approach. Remarkably, GO was directly functionalized by GPTMS in the stirring process at 100°C. In the following preparation procedure of the GO-modified CFRP composites, the solvent did not need to be removed and could be directly used in the next step, which is facile and environmentally friendly.

The main aim of this work is to prepare silane functionalized GO-modified epoxy resin and the CFRP composites by a convenient method. The effect of GO content on tensile strength and monofilament interfacial shear strength of CFRP composites was investigated. Moreover, considering the currently reported researches mainly focus on the

mechanical property improvement of the composites after the introduction of GO, while the fracture process is rarely analyzed [36–38]. In our research, the fracture process of the modified CFRP composites was intuitively observed and analyzed by the digital image correlation (DIC) system. To understand the reinforcing mechanism of GO, the fractured surface of epoxy resin and CFRP composites was investigated by scanning electron microscopy (SEM).

2. Materials and Experimental

2.1. Materials. The epoxy resin of E51 and 711 were procured from Nantong Xingchen Synthetic Material Co. LTD. and Tianjin Jingdong Chemical Composite Material Co. LTD., respectively. Graphene oxide (GO) (Oxygen content: 46–49 wt.%, ash: ≤ 0.1 wt.%) was made by Shanxi Institute of Coal Chemistry, Chinese Academy of Sciences according to the modified Hummer's method. The optical photograph of the GO powder and its solution state is shown in Figure 1. Silane coupling agent 3-glycidoxypropyl trimethoxysilane (GPTMS, 97%) with a relative molecular weight of 236.34, was obtained from Shanghai Aladdin Biochemical Technology Co. LTD. Acetone (AR grade) was from Sinopharm Chemical Reagent Co. LTD. Diaminodiphenylmethane (DDM) as curing agent procured from Shanghai Sanaisi Reagent Co. LTD. 2-ethyl-4-methylimidazole as accelerator was procured from Lianlongbohua (Tianjin) Pharmaceutical Chemistry Co. LTD. All the chemicals were used without further purification. T800 carbon fiber (12K) with an average diameter of 5 μm was from Shanxi Steel Carbon Material Co. LTD. The index of T800 carbon fiber is as follows: tensile strength 5.5 GPa, tensile modulus 294 GPa, elongation 1.9%, and density 1.81 g/cm^3 .

2.2. Preparation of GO-Reinforced Epoxy Resin Specimen. The GO was firstly dispersed in acetone solution by ultrasonication for 1 hour and then mixed with silane coupling agent GPTMS by stirring for 5 hours at 100°C (1000 r/min). Subsequently, the mixture of GO and epoxy resin (with a little acetone) was mixed by ultrasonication for 2 hours and stirred for 4 hours at 100°C (800 r/min). The doping amount of GO in epoxy resin varied from 0.05 to 0.6 wt.%. The excess acetone from a GO-epoxy mixture was removed through continuous stirring in the heating jacket at 130°C. After that, the curing agent and accelerator were added to the epoxy resin and the ratio of the curing agent, epoxy resin, and accelerator was 25:100:1 ~ 1.5. The mixture was stirred for 15 min and vacuum defoamed for 15 min. Finally, the mixture was poured into the steel mold for curing at a stepwise increasing temperature from 90°C (1 h) to 120°C (2 h) and 150°C (3 h) to obtain the resulting GO modified epoxy resin.

2.3. Preparation of GO-Modified CFRP Composites. The as-prepared modified epoxy resin above with different GO fractions was used to fabricate the CFRP composites. As schematically displayed in Figure 2, T800 carbon fibers were placed on the roller and a total of 8 layers of unidirectional

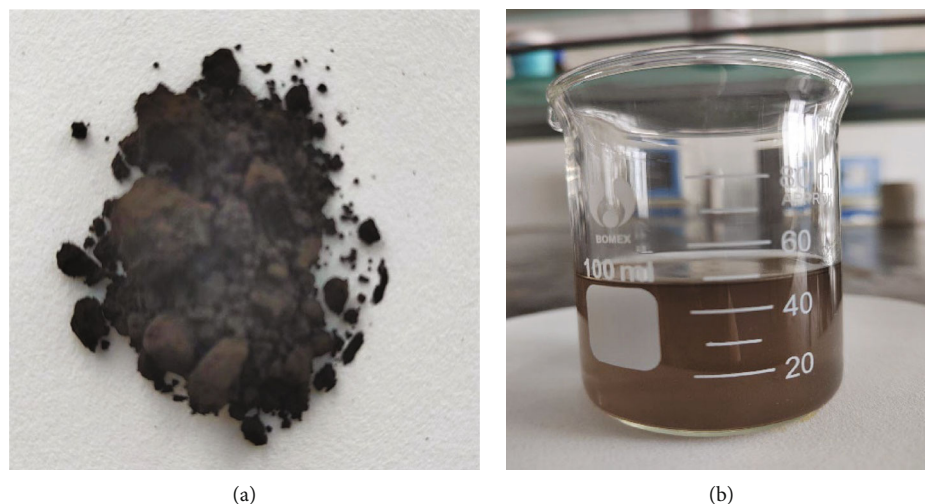


FIGURE 1: The photograph of GO: (a) GO powder; (b) GO solution dissolved in acetone (The concentration of 0.1%).

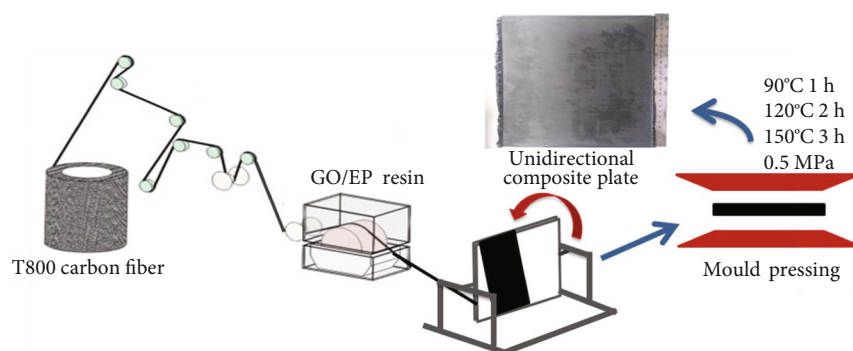


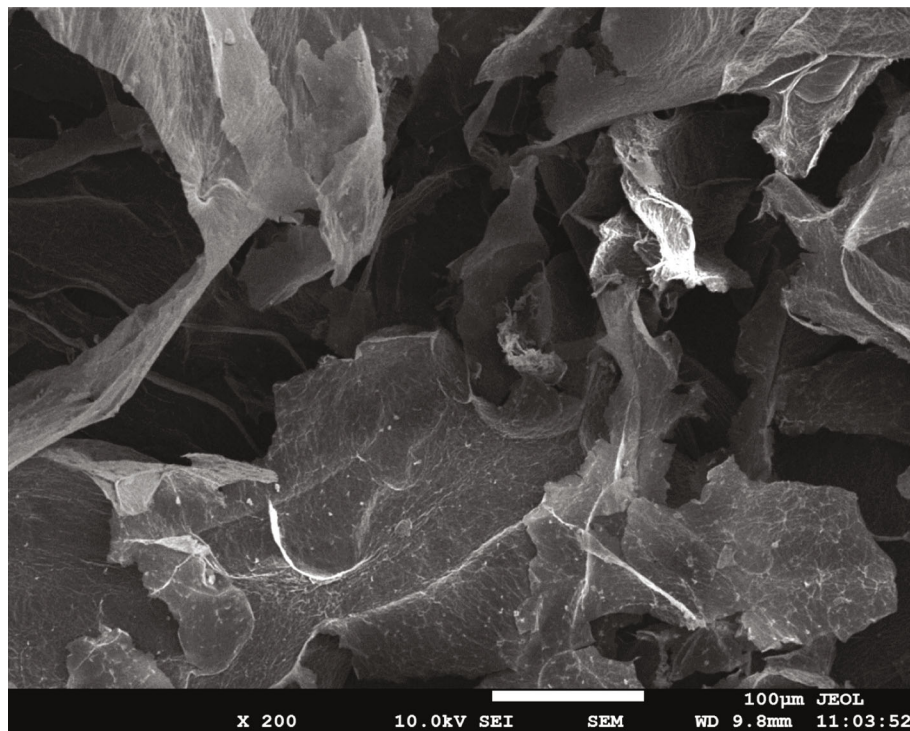
FIGURE 2: The schematic diagram of the preparation process for the GO-modified CFRP composites.



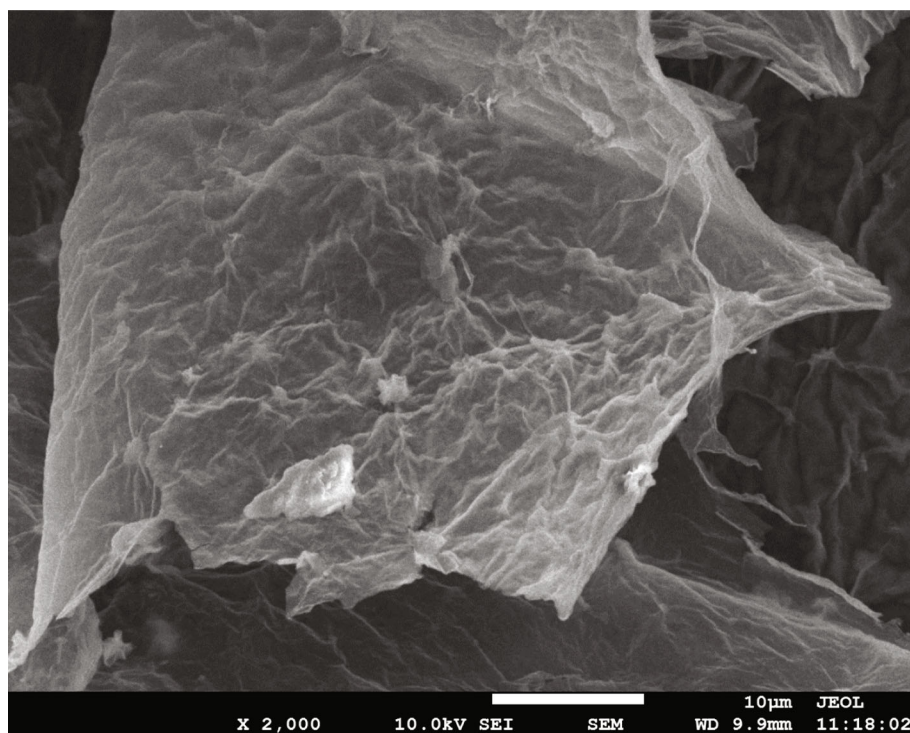
FIGURE 3: The photograph of the test setups (a) Tensile machine and DIC system; (b) composite interface evaluation device.

carbon fiber plate were prepared through the winding process. The pressure of 0.5 MPa was unremittingly applied during the curing process to get the desired CFRP composites.

2.4. Characterization. Fourier transform infrared spectrum (FT-IR, Vertex 80 V, Bruker Co., USA) was performed under radiation ranging from 500 to 4000 cm^{-1} to evaluate surface functional groups of GO. Scanning electron microscopy



(a)



(b)

FIGURE 4: SEM images of GO.

(SEM, JSM7001F) was applied to characterize the morphology of GO, the fractured surface of modified epoxy resin and the CFRP composites. The tensile and flexural properties of GO-modified epoxy resin were assessed according to GB/T 2567-2008, and the test rate was 2 mm/min. The tensile

specimen size was 200 mm × 10 mm × 4 mm, and the flexural specimen size was 95 mm × 15 mm × 4 mm. The tensile properties of the CFRP composites were assessed according to the standard GB/T 3354-2014. The size of the CFRP strip specimen for tensile testing is 220 mm × 12 mm × 1.2 mm, and the

stretching rate was 2 mm/min. An average of five specimens is used for each mechanical test to obtain the final results. Three-dimensional strain test was proceeded by a digital image correlation (DIC) system (Figure 3(a)).

Monofilament interfacial shear strength (IFSS) was estimated by a composite interface evaluation device (HM410) shown in Figure 3(b), and the IFSS values were calculated as per the following equation [23]:

$$\tau_{\text{IFSS}} = F_{\text{max}} / \pi D_f L_e \quad (1)$$

where F_{max} is the maximum load, D_f is the monofilament diameter of carbon fiber, and L_e is the embedding length of resin droplets. 25 valid values were averaged to obtain the final values of IFSS.

3. Results and Discussion

3.1. Morphology and Chemical Composition of GO. The morphology of GO was investigated by SEM observation. It can be seen from Figure 4(a) that the two-dimensional feature and sheet-like structure of GO are distinctive. The as-obtained GO has high quality with favorable dispersibility and very thin stacking of graphitic layers. From the magnified SEM image shown in Figure 4(b), the coarse surface rich in wrinkled structure is further revealed. These rough wrinkles in Figure 4(b) stem from the oxygenated functionalities on the surface of GO [27]. These wrinkled structures can maintain a stable existence of GO by diminishing surface energy, which is considered an excellent interface for combination with the polymer network [39].

Functional groups present on the surface of GO were evaluated by the FTIR spectrum, as shown in Figure 5. As can be seen, the characteristic peaks of GO emerged at 3400 cm^{-1} , which is attributed to the stretching vibration of hydroxy groups. Moreover, peaks at 1730 cm^{-1} , 1620 cm^{-1} , 1388 cm^{-1} , and 1053 cm^{-1} correspond to the stretching vibration of C=O, C=C, C-C, and C-O, respectively. It is worth noting that the existence of hydroxy and carbonyl vibration peaks in the FTIR spectrum of GO indicates that the oxygen-containing functional groups (hydroxyl and carboxyl) are successfully introduced to the surface of GO, which is beneficial to the dispersion of GO in epoxy resin.

3.2. Mechanical Properties of GO-Modified Epoxy Resin Specimen. The influence of the GO incorporation on the mechanical properties of epoxy resin was evaluated by tensile and bending tests. The results are shown in Figure 6. As observed in Figure 6(a), the tensile strength and elongation of the specimen are improved obviously with the increase of GO content in epoxy resin. Without GO, the tensile strength of epoxy resin is 81.2 MPa and the elongation at break is 5.2%. After the addition of GO in epoxy resin, the mechanical properties show an upward trend. At the GO content of 0.1 wt.%, tensile strength increases to 85.6 MPa and the elongation ratio increases to 6.9%, which increases by 5.4% and 32.7%, respectively, when compared with pure epoxy resin. Moreover, the tensile modulus of epoxy resin with 0.1 wt.% GO content is increased by 7.7%. The

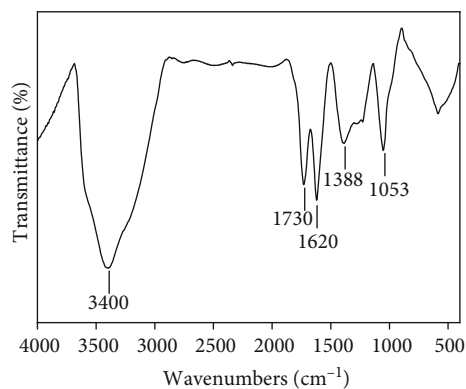


FIGURE 5: FTIR spectra of GO.

improvement can be attributed to the 2D sp^2 carbon-based structure of GO with intrinsic high mechanical properties [27]. Nonetheless, as the GO content further increases, the tensile strength and elongation decrease continuously, and the tensile modulus gradually increases. Especially, when the GO content reaches 0.6 wt.%, the tensile property of the epoxy resin specimen is lower than that of the unmodified resin. The property deterioration is attributed to the poor dispersion of excess GO in the epoxy resin. The agglomerated GO will cause stress concentration in the epoxy resin. It induces the initial generation and propagation of the microcracks in the specimen, which affects the mechanical properties of epoxy resin [29].

The bending strength and bending modulus of the epoxy resin specimen were evaluated under the three-point-loading conditions. The results illustrated in Figure 6(b) reveal the same tendency as the tensile strength. Without the addition of GO, the bending strength of the pristine epoxy resin specimen is 125.2 MPa. When the GO content reaches 0.1 wt.%, the bending strength increases to 139.4 MPa, which increases by 11.3% compared with pristine epoxy resin. In addition, the bending modulus of epoxy resin with 0.1 wt.% GO content is increased by 4.8%. However, with the GO content further increasing, bending strength decreases continuously, which is consistent with the previous reports. Shen et al. [40] found that the agglomeration effect of GO was obvious when the amount of GO surpasses 0.1 wt.%. It will adversely affect the toughening modification of epoxy resin. Therefore, when the concentration of GO is 0.05~0.1 wt.%, the comprehensive performance of the composite materials is superior.

3.3. Tensile Properties of GO-Modified CFRP Composites. Through the study of the mechanical properties of GO-modified epoxy resin, it is found that the mechanical properties of epoxy resin are better when the GO content is 0.05 wt.% and 0.1 wt.%. Therefore, GO-modified CFRP composites with GO content of 0.05 wt.% and 0.1 wt.% were prepared. Meanwhile, the unmodified CFRP composite was prepared as a comparison. The variation in tensile strength with the increased GO content in CFRP composites and stress versus strain curves are provided in Figures 7(a) and 7(b), respectively. As observed, the incorporation of GO

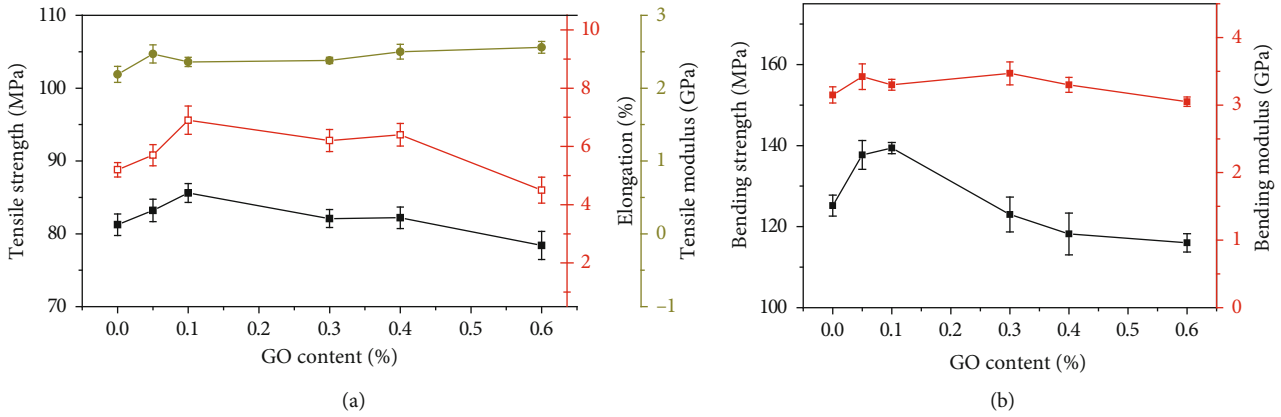


FIGURE 6: Variation in tensile strength, tensile modulus and elongation at break (a) and bending strength and bending modulus (b) with the increasing GO content in epoxy resin.

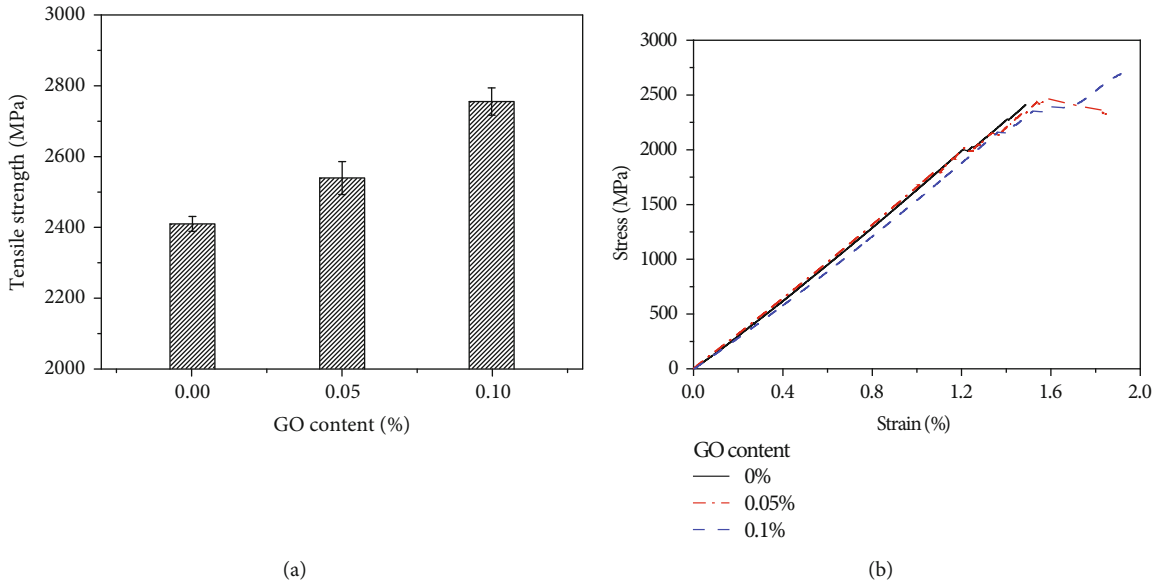
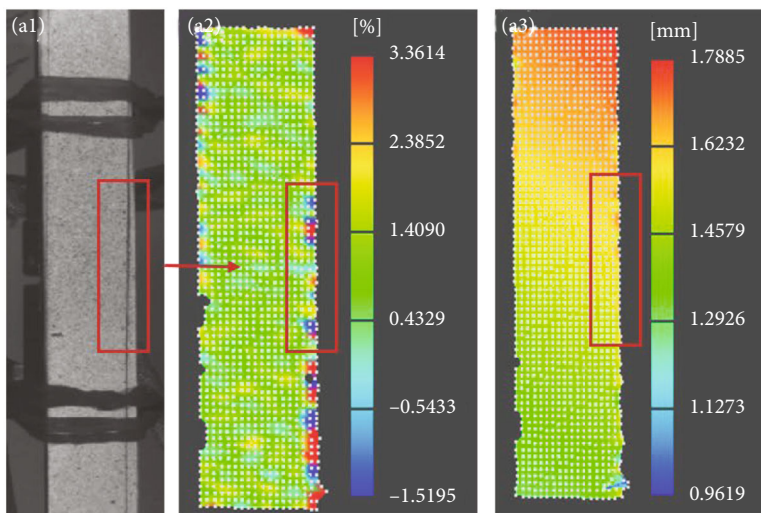


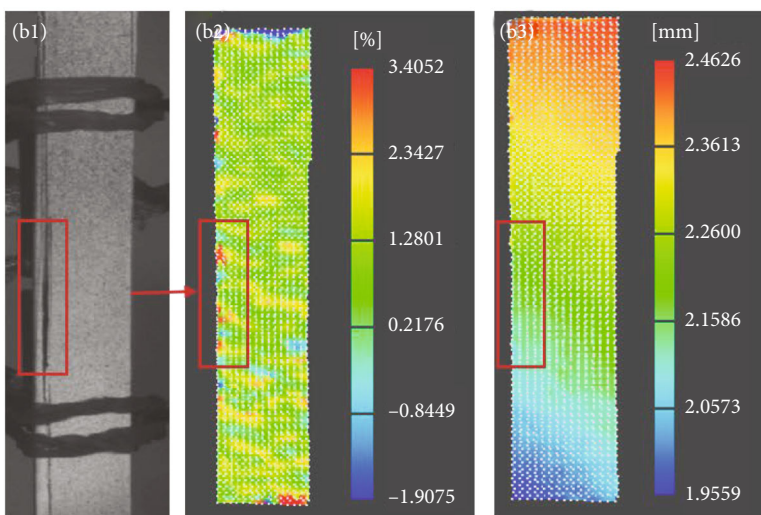
FIGURE 7: (a) variation in tensile strength and (b) stress vs. strain with the increased GO content in CFRP composites.

has a positive impact on the tensile properties compared to the neat CFRP composites. The tensile strength of CFRP composite without GO modification is 2410 MPa, while after the GO addition in epoxy resin, the tensile property of the CFRP composites shows an upward trend. At the GO contents of 0.05 wt.% and 0.1 wt.%, the tensile strength increases to 2540 MPa and 2756 MPa, which increases by 5.4% and 32.7%, respectively, compared with the unmodified CFRP composites. The results indicate that a low amount of GO can effectively improve the tensile properties of CFRP composites. It attributes to a large number of hydroxyl and carboxyl active functional groups on the surface of GO. The active functional groups can not only make the GO more evenly dispersed in the resin matrix, but also interact with the epoxy resin to produce a compact interface association. It also benefits for the formation of a favorable interface between the carbon fibers and the doped epoxy resin, which effectively prevents crack propagation and improves the interface performance.

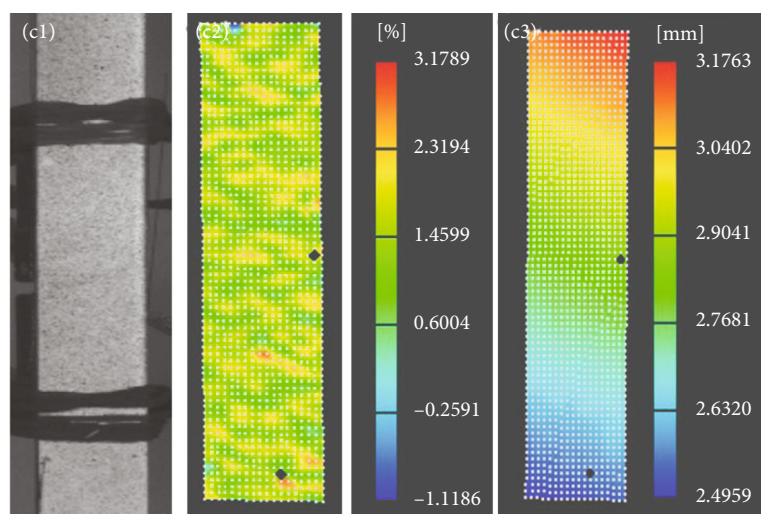
To further study the fracture process of the CFRP composites, the digital image correlation system was used to monitor the tensile test process. Figure 8 shows the distribution of longitudinal strain and displacement of CFRP composites during the tensile process. Obvious longitudinal cracks can be observed at the initial stage of fracture on the surface of CFRP composites without GO. The distribution of longitudinal strain and displacement is not uniform, which signifies obvious stress concentration. When the content of GO is 0.05 wt.%, the stress concentration phenomenon is still observed in the three-dimensional strain diagram. However, the stress concentration phenomenon is significantly reduced compared with the unmodified CFRP composites. When 0.1 wt.% GO is added, no longitudinal cracks are observed at the initial stage of fracture. The longitudinal strain and displacement distributions are uniform, indicating that there is no obvious stress concentration. The result demonstrates that the addition of GO can improve the stress concentration of CFRP composites.



(a) GO 0% strain

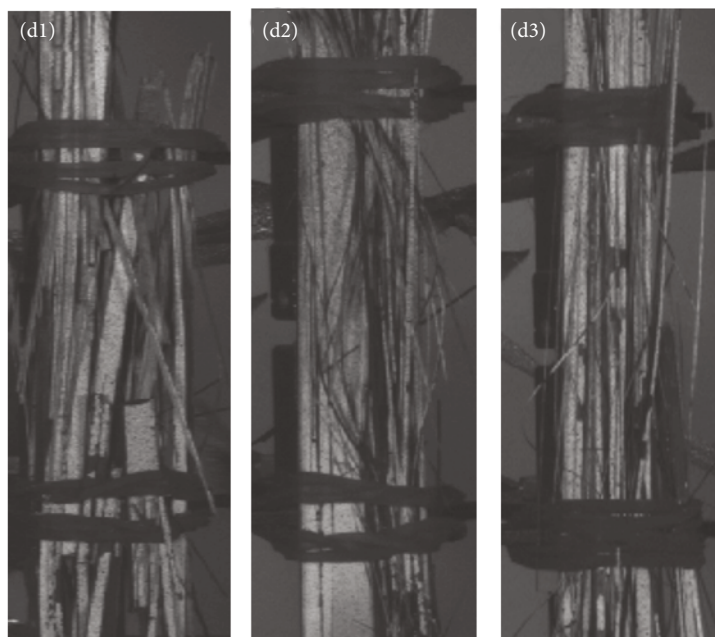


(b) GO 0.05% strain



(c) GO 0.1% strain

FIGURE 8: Continued.



(d) Fracture morphology (d₁:GO 0%; d₂:GO 0.05%; d₃:GO 0.1%)

FIGURE 8: Three-dimensional strain test results of GO-modified CFRP composites (a1, b1, and c1: Sample morphology during the tensile process; a2, b2, and c2: longitudinal strain; a3, b3, and c3: longitudinal displacement; d1, d2, and d3: Sample morphology at tensile fracture moment).

Moreover, as the stress concentration always occurs in the region where the sample is prone to fracture, the addition of GO can effectively improve the tensile properties of the CFRP composites.

3.4. Interfacial Properties of GO-Modified CFRP Composites.

The mechanical properties of the CFRP composites also depend on the interfacial interaction of fibers and the epoxy resin matrix. To explore the effect of GO on the properties of the fiber/epoxy interphase, microbonding tests were conducted. The results of the IFSS of CFRP composites with the increase of GO content are provided in Figure 9. As is expected, the IFSS of CFRP composites is enhanced after the addition of GO in epoxy resin. Especially, the CFRP composite with 0.1 wt.% concentration of GO manifests the highest IFSS. Without the addition of GO, the IFSS of CFRP composite is 25.83 MPa. While after the 0.05 wt.% and 0.1 wt.% addition of GO, IFSS increases to 26.8 MPa and 29.06 MPa, which increases by 3.8% and 12.5%, respectively, compared with the unmodified CFRP composites. It is attributed to the abundant oxygenic functional groups on GO which exerts polarity and good dispersion as well as effective bonding between GO and resin matrix. At the same time, the polar groups on the GO's surface can also react with the active groups on the surface of carbon fibers. As a result, favorable interfacial adhesion with epoxy resin comes into an "interlock effect". Therefore, the addition of GO not only elevates the mechanical properties but also effectively improves the interface bonding of the CFRP composites.

3.5. Microstructure of GO-Modified Epoxy Resin and CFRP Composites.

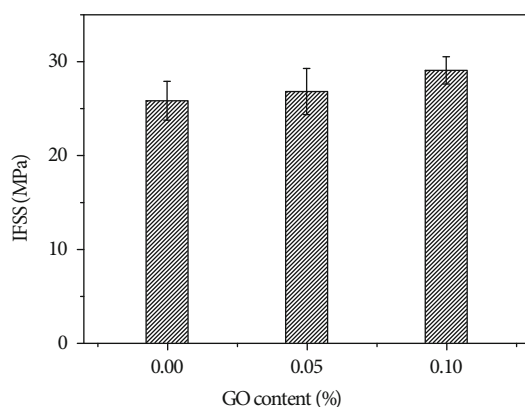
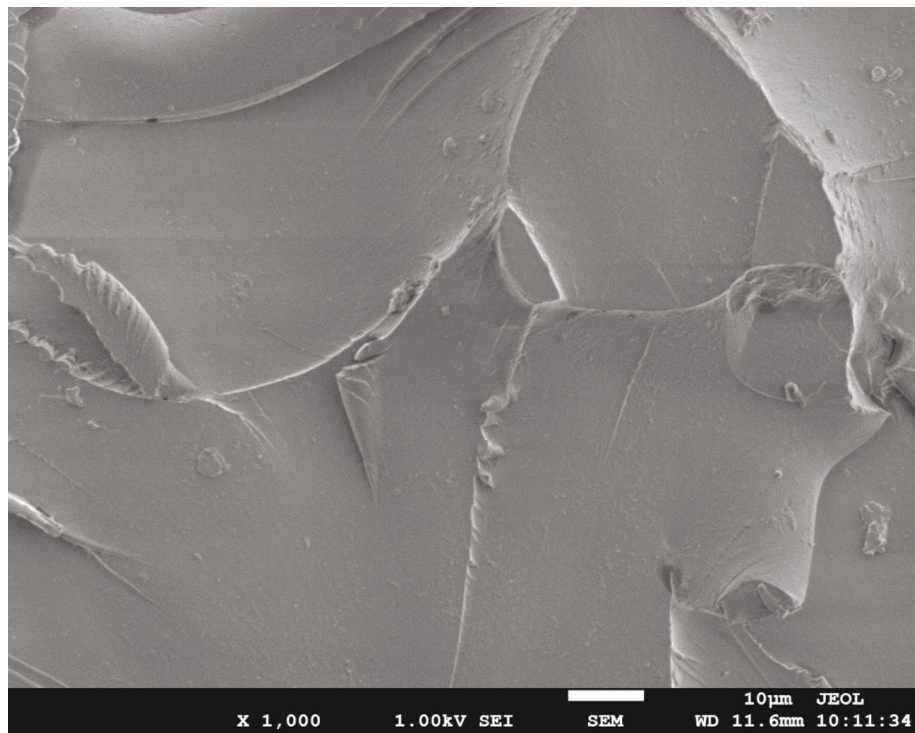
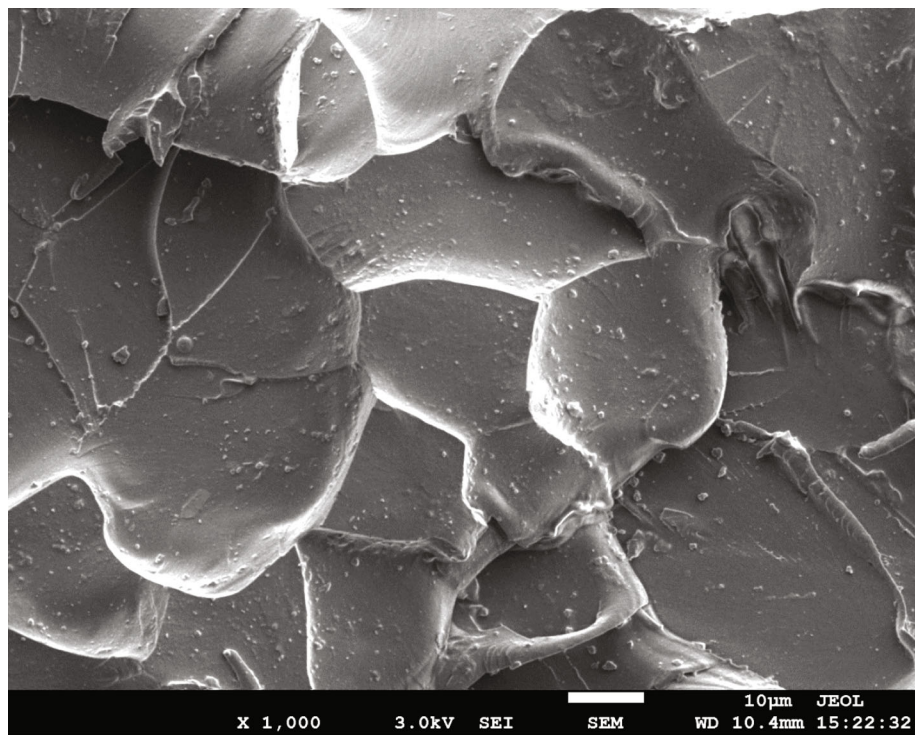


FIGURE 9: IFSS variation of CFRP composites with the increase of GO content.

nism of GO addition, the fracture surface of epoxy resin specimens is observed by SEM, as shown in Figure 10. One can see the cracks on the surface of the pristine epoxy resin are smooth, indicating the low crack propagation resistance. The behavior is consistent with a brittle fracture mode. In contrast, in the case of modified epoxy resin with 0.05 wt.% GO addition, the fracture section becomes relatively coarser and the cracks increase significantly, which indicates that the fracture mode of the material evolves from brittle fracture to ductile fracture, as shown in Figure 10(b). With the further increase of the GO content to 0.1 wt.%, it can be observed that the crack direction becomes a disorder and the thickness of the crack is not uniform. Moreover, the fault surface presents layers of overlapping, as shown in the part marked

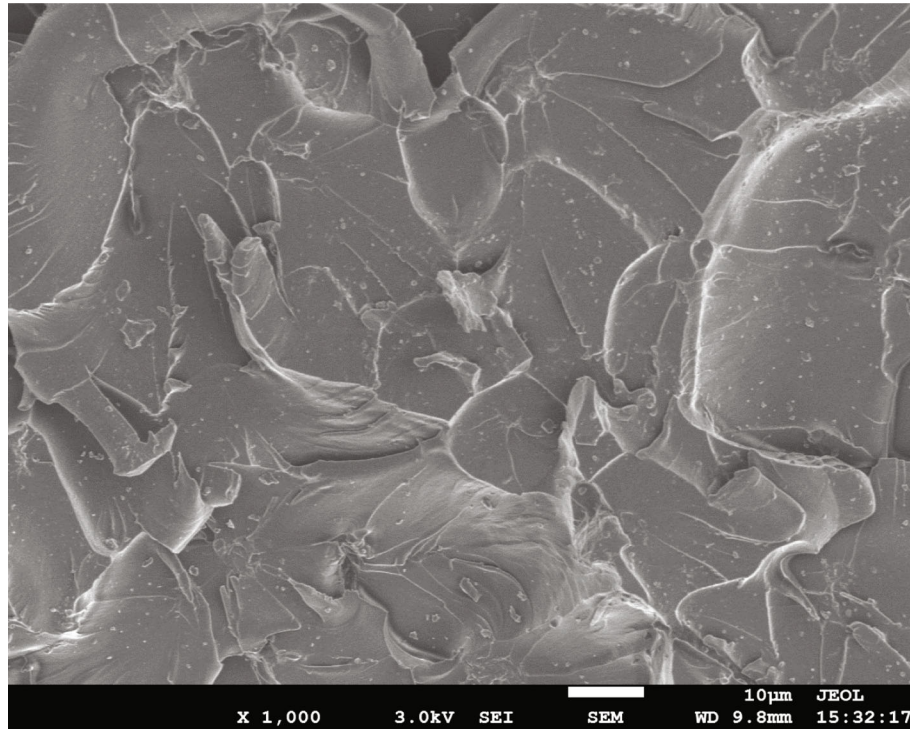


(a)

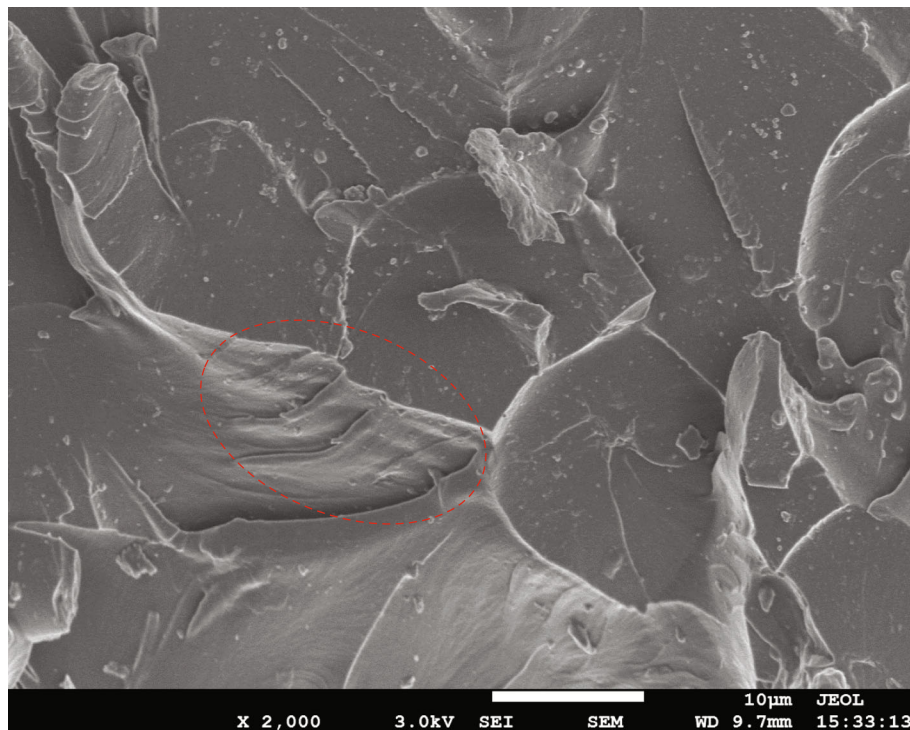


(b)

FIGURE 10: Continued.



(c)



(d)

FIGURE 10: SEM images (a): pure epoxy resin specimen; (b): 0.05 wt.% GO-epoxy resin specimen; (c, d): 0.1 wt.% GO-epoxy resin specimen.

in red in Figure 10(d). It attributes to the high strength and high modulus of graphene, which results in the crack deflect or bifurcate along the epoxy resin adhered to graphene when the crack encounters graphene. As a result, the entire failure path is prolonged and the propagation area and distance of

the fracture crack are increased. In addition, a large number of oxygenic functional groups on the surface of GO make GO and epoxy resin bond together, resulting in chemical bonding. The interface bonding between GO and epoxy resin is strong, which can consume more external loading

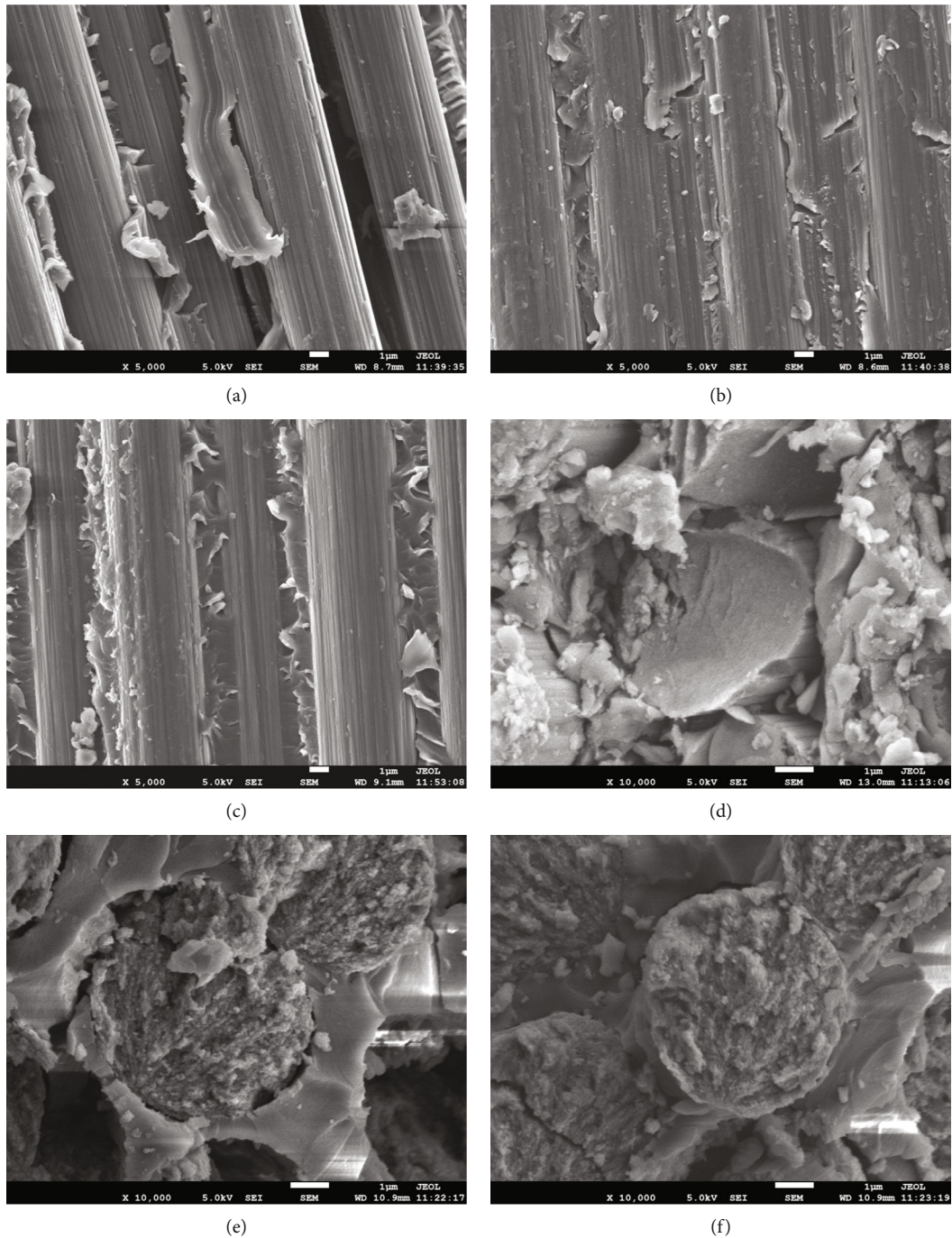


FIGURE 11: SEM images (a), (d): pure CFRP composite; (b), (e):0.05 wt.% GO-CFRP composite; (c), (f):0.1 wt.% GO-CFRP composite.

energy and further achieve the strengthening and toughening of epoxy resin [41].

Fracture surface images of CFRP composites are presented in Figure 11. It can be observed from Figures 11(a) and 11(d) that the damage of CFRP composites mainly occurs along the interface between fibers and resin matrix. The fiber surface after the damage is relatively smooth, and the resin is observed to peel off from the fiber surface with less resin coated on the fiber surface, indicating weak interfacial interactions between resin and the fibers. While in

the case of 0.05 wt.% GO modified composites, it can be observed (Figures 11(b) and 11(e)) that there are resin coating and adhesion on the fiber surface, but some resin is still detached from the fiber surface. Moreover, the resin between carbon fibers contains more fold morphology than the unmodified CFRP composites, which leads to a longer path of fiber breakage for samples and absorbs more energy during the interface damage. In the case of CFRP composites with 0.1 wt.% GO modification, the adhesion between fibers and resin is tighter, and no obvious resin peeling is observed,

as shown in Figures 11(c) and 11(f). It is a clear indication of enhanced interfacial interaction between the fibers and resin matrix.

In addition, the SEM images show that when the GO content is 0.1 wt.%, the interfacial interaction and bonding condition between the fibers and epoxy resin are favorable. It will further enhance the loading transfer from resin to fibers and reduce the growth rate of the microcracks. As a result, GO-modified CFRP composites show significant improvement in mechanical strength when compared to pristine CFRP composites [42]. This result is in agreement with the previous research results on the tensile and interfacial properties of CFRP composites.

4. Conclusions

In summary, a facile and efficient method to prepare GO-modified epoxy resin and CFRP composites has been explored. The effect of GO content on the mechanical and interfacial properties was investigated. The following outcomes have been taken from the experiment results:

- (i) The modified epoxy resin with 0.1 wt.% GO addition presents the best mechanical properties. The tensile strength, tensile modulus, and elongation at break of epoxy resin increase by 5.4%, 7.7%, and 32.7%, respectively
- (ii) Compared with the pristine CFRP composites, the tensile strength and monofilament interfacial shear strength of the modified CFRP composites with 0.1 wt.% GO addition increased by 14.4% and 12.5%, respectively
- (iii) The prominent improvement in mechanical and interfacial properties is attributed to the hydroxyl and carboxyl active functional groups on the surface of GO, which can not only enhance the dispersity of GO in the resin matrix but also interact with epoxy resin to produce a compact interface association
- (iv) The digital image correlation strain experiments demonstrate that the addition of GO can significantly improve the stress concentration of CFRP composites and enhance the tensile properties. The SEM analyses confirm that the addition of GO can make the crack deflect or bifurcate along the epoxy resin matrix adhered to graphene

The thermal, dynamic thermomechanical properties and low-temperature resistance of GO-modified CFRP composites will be investigated in future works to ensure the stable and reliable application of GO-modified CFRP composites.

Data Availability

The data used to support the findings of this study are included within the article. Further data or information is available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

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