Interfacial Improvement of Carbon Fiber/Epoxy Composites by Incorporating Superior and Versatile Multiscale Gradient Modulus Intermediate Layer with Rigid-flexible Hierarchical Structure

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Abstract In order to enhance the interfacial adhesion of carbon fiber (CF) and polymer matrix, a multiscale gradient modulus intermediate layer with rigid-flexible (GO-PA) hierarchical structure was designed and fabricated between CFs and matrix by a facile and businesslike strategy. The polarity, roughness and wettability of CF surface as well as the thickness of intermediate layer in composite have been significantly increased after rigid-flexible hierarchical structure was constructed. The IFSS, ILSS, compression and impact toughness manifested that the hierarchical structure could bring about a fantastic improvement (76.8%, 46.4%, 40.7% and 37.8%) for the interfacial and mechanical properties than other previous reports. Consequently, the establishment of CF surface with gradient modulus rigid-flexible hierarchical structure via regulation of nanoparticles and polymer array would open a new, viable and promising route to obtaining high-performance composites.

Keywords Carbon fibers; Polymer-matrix composites; Interface; Hierarchical structure; Gradient modulus

INTRODUCTION

Polyacrylonitrile (PAN) based carbon fiber (CF) reinforced polymer composites (CFRPs) are extensively applied in defense weapon, aerospace, ocean exploration and automobiles due to the high rigidity, high specific strength and modulus, light weight, easy processing and high temperature resistance.[1–6] The interfacial adhesion between CF and epoxy matrix is vital to the whole mechanical properties of CFRPs because outstanding interphase could ensure the stress transfer evenly and prevent further crack growth. Nevertheless, the smooth surface, non-polarity and chemical inertia of CF surface resulted in poor adsorption and wettability between fiber and matrix, and the stress cannot ensure uniformly transferred from matrix to CFs, leading to weak interfacial strength of composites. In addition, the modulus disparity between CF and matrix might cause stress concentrations at the interface layer, which also affected internal stress shift efficiency from the matrix to CFs.[7–9] In recent years, many scientific studies have been reported to embellish CF surface to enhance the interfacial bonding between fibers and epoxy, such as plasma treatment,[10] chemical grafting,[11,12] coating,[13,14] and in situ polymerization.[15] The incorporation of macromolecules or nanoparticles into the interphase have demonstrated to be a neoteric and valid method.[16,17] Notably, incorporation of typical two-dimensional graphene oxide (GO)onto the CF surface via branched macromolecules or coupling agents (PAMAM, HDI, TEPA) to form a hierarchical enhancement structure has been proven to be an effective approach to improving the overall mechanical properties of CFRPs.[18–20] Li et al.[18] have confirmed that the surface energy increased significantly after chemical grafting of GO onto CF via poly(ami-dom amine) dendrimers. Wu et al.[20] have reported that chemically grafting GO onto the CF surface with tetraethylenepentamine (TEPA) as a bridging agent, the interlaminar shear strength (ILSS) of composites was improved by 48.5%. However, the existing scientific problems were as follows. (1) The steric hindrance effect of branched macromolecules resulted in low grafting density of GO and uncontrollable spatial arrangement of GO on CF surface, which limited the mechanical interlocking, chemical bonding interaction and compatibility between CFs and epoxy; (2) The optimal modulus matching has not been achieved since the modulus of GO was much higher than that of matrix, and the stress was difficult to com-
pletely eliminate in the interface area in time. Therefore, the above problems would restrict the further improvement of composite interfacial properties.

If GO and macromolecules were successively introduced onto CF surface to construct a novel hierarchical structure, GO would not be affected by steric hindrance, and more GO could orderly graft onto CF surface and increase the specific surface area of CF, which would also serve as bridge to link more macromolecules chains. They could provide anchors and active sites to increase the mechanical interlocking, chemical bond and compatibility with epoxy. Moreover, the nacre-like hierarchical structure incorporation of adequate rigid component and soft flexible chain was beneficial to the formation of gradient modulus intermediate layer, which could balance the modulus of fiber and matrix to achieve the best matching. As far as the author knows, the influence of hierarchical rigid-flexible structure (GO-macromolecules) on the interfacial adhesion of CF/epoxy composites has not been investigated.

In this work, GO and polyamide (PA) were successively incorporated onto CF surface by simple esterification and anionic polymerization reaction to build a hierarchical reinforcement structure, as shown in Fig. 1. The morphologies and chemical components of multi-scale blended reinforcements were validated by SEM, TEM, XPS and Raman spectra. The wettability of CF with epoxy matrix and interphase thickness of composites were estimated by dynamic contact angle analysis (DCA) and energy dispersive spectroscopy (EDS). The interfacial adhesion properties, overall mechanical properties and the enhancement mechanism of CF-GO-PA/epoxy composites were also studied. It could be prospective that the hierarchical reinforcement structure with gradient modulus in the fiber-matrix interface could play the role of fracture energy transfer and change the propagation path of the crack to obtain a high-performance CFRPs.

EXPERIMENTAL

Raw Materials

The commercial CF (T300, density of 1.76 g·cm\(^{-3}\)) were supplied by Sino steel Jilin Carbon Co. Graphite powder was bought from Huayuan Chemical Co., Ltd., Shanghai Huayi Group. Caprolactam (CPL), and adipoyl chloride were provided by Aladdin Co., Shanghai, China. Potassium persulfate (\(K_2S_2O_8\)) and
silver nitrate (AgNO₃) were obtained from Sinopharm Chemical Reagent Co., Shanghai, China. Other chemicals, including N,N-
dimethylformamide (DMF), tetrahydrofuran (THF), acetone, and
ethanol used as a solvent, were supplied by Tianjin Bodi Organic
Chemicals Co., Ltd.

**Surface Treatment of CF and Oxidation of Graphite Powder**
The CF was refluxed in an acetone solution at 80 °C for 48 h to
remove polymer sizing and was denoted as pristine CF. Then,
the pristine CF was oxidized at 70 °C for 1 h in 0.01 mol·L⁻¹
AgNO₃/0.1mol·L⁻¹ K₂S₂O₅ solution to introduce carboxyl groups
(CF-COOH), which was refluxed in a saturated solution of LiAlH₄-
THF at 60 °C for 2 h to produce hydroxyl groups on CF surface
(CF-OH). GO was synthesized by graphite oxidation based on
a modified Hummers’ method.[20]

**Construction of Hierarchical Structure onto CFs**
**Surface**
GO (0.2 g) was mixed with 80 mL of DMF and sonicated for 8 h
and was heated to 70 °C for 30 min. CF-OH (0.4 g) and a few
drops of H₂SO₄ was added to the three-necked flask as a
reactant, and then the mixed solution of GO was added, refluxed
at 70 °C for 12 h. The CF-GO was taken out and rinsed with DMF
and ethanol.

CF-GO (0.4 g) was added to excess adipoyl chloride (6.65 mL) and immersed in a toluene solution, and refluxed at
100 °C for 4 h protected by N₂. Subsequently, 5.56 g of CPL
was added to the reaction system and further continued for 4 h
to gain CPL terminated-stabilized CF-GO, which was then
dried. Finally, 80 g of CPL was heated to 120 °C at 0.1 MPa and evaporated to no bubbles. Then, 0.24 g of NaOH
(mass ratio of CLNaOH=1.0.003) was added to the molten
CPL, and vacuuming continued until no bubbles, and the
temperature raised to 140 °C and kept for 30 min. The CPL
terminated-stabilized CF-GO was placed in the reaction solution,
heated at 140 °C and rapidly heated to 150 °C in 30 min, and then
the mixture was stirred for 24 h. Then, the solution was
filtered and alternately washed by formic acid and deionized
water to obtain PA-grafted CF-GO (CF-GO-PA),[23] which was
then dried in a vacuum oven at 80 °C.

**Fabrication of CF/Epoxy Composites**
CF/epoxy composites were manufactured with the unidirec-
tional fiber prepreg by compression molding and could be
divided into the following two steps. (1) The preparation
procedure of resin matrix: epoxy resin (E-51) and curing agent
(H-256) (mass ratio of CL:NaOH=1:0.003) was added to the molten
CPL, and vacuuming continued until no bubbles, and the
speed was 2 mm·min⁻¹. (2) the resin-impregnated CF was placed in a stainless steel mould and preheated to 90 °C
and then maintained 2 h under 5 MPa, then pressurized to 10
MPa, heating up to 120 °C for 2 h, followed by curing at 150 °C
for 3 h and then cooled solidification for 12 h. The fiber content
in the composite was controlled at about 68±1.5%.

**Characterization**
X-ray photoelectron spectroscopy (XPS, Thermofisher Scienci-
cific, USA) and Raman spectroscopy (RM2000) were used to
measure the chemical composition and structure composition
of functionalized CF surface. The thermo-gravimetric analysis
(TGA, DTG60H) was used to investigate the thermal stability
behaviors of fibers to obtain the grafting amount of GO and
PA6 on CFs surface in the range of 30–700 °C at the heating rate
of 10 °C·min⁻¹ in nitrogen atmosphere. Field-emission scanning
electron microscopy (FESEM, Hitachi S-5700) and transmission
electron microscope (TEM, JEM-2100F) were adopted to
characterize the CFs surface topographies; EDS (JEOL JSM-
5900LV) equipped on SEM was to evaluate the interfacial
microstructures between CF and matrix. All samples needed to
spray gold to improve the conductivity.

Dynamic contact angle meter (DCA, DCAT21, Germany)
was measured to investigate the wettability of CF surface. Po-
lar deionized water and nonpolar diiodomethane were used as
the testing liquids. The surface energy, polar component and
dispersive component of different fibers were calculated
according to the following formula:

\[
\gamma(1 + \cos \theta) = 2\sqrt{\gamma_f \gamma_d} + 2\sqrt{\gamma_p \gamma_d}
\]

(1)

\[
\gamma_f = \gamma_p + \gamma_d
\]

(2)

where \( \gamma_f \) and \( \gamma_d \) were the surface tension of testing
immersion liquid, its dispersive and polar components,
respectively.

The interfacial shear strength (IFSS) was adopted to calcu-
late the interfacial performance between CFs and matrix by
the monofilament debonding test (FA620, Japan). Epoxy resi-
in (E-51) and curing agent (H-256) were mixed to prepare mi-
crodroplets, which were cured at 90 °C for 2 h, then at 120 °C
for 2 h and eventually at 150 °C for 3 h. The fiber was pulled
out from the microdroplets, and each final result was from the
average value of five specimens. The value of IFSS could be
calculated by solving the following equation:

\[
IFSS = \frac{F}{\pi d h}
\]

(3)

where \( F \) was the maximum pullout force, \( d \) was the CF average
diameter, and \( h \) was the embedded length of a single filament.

The ILSS of CF/epoxy composites was measured using a
three-point short-beam bending performed on a general ma-
terial testing machine (GT-7000-A2X, Taiwan, China) based
on ASTM2344 method. The ILSS value could be obtained by
solving the following formula:

\[
ILSS = 0.75 \times \frac{F_{max}}{bh}
\]

(4)

where \( F_{max} \) was the maximum compression load at fracture (N),
\( b \) and \( h \) were the width of the sample (mm) and thickness of
the specimen (mm), respectively.

Axial compressive strength (δ) of CF/epoxy composites was
carried out using a general material testing machine, the speed
was 2 mm·min⁻¹, and the sample size was 12 mm × 6
mm × 2 mm. All test results depended on the average of
five samples. The δ value was calculated according to the
equation:[24]

\[
\delta = \frac{P}{wh}
\]

(5)

where \( P \) represented the maximum load (N) before failure, \( w \) and \( h \) represented the sample width (mm) and thickness (mm),
respectively.

Impact properties of CF/epoxy composites were conduc-
ted on a drop-weight impact test system (9250HV, Instron,
USA). The specimen size was 55 mm × 6 mm × 2 mm, and the
impact span was 40 mm. Each reported date was gained from

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the average value of five efficient tests.

**RESULTS AND DISCUSSION**

**Surface Morphologies of Functionalized CF**

The CF surface roughness was observed by SEM, as depicted in Figs. 2(a)–2(c). The pristine CF surface (Fig. 2a) was glossy and tidy with some narrow grooves. For CF-GO (Fig. 2b), the GO sheets with a larger specific surface area adhered closely to the CF surface along the axial direction, which would provide more active sites and mechanical points for the resin. For the morphology of CF-GO-PA (Fig. 2c), the CF surfaces and GO sheet surfaces were all uniformly covered by polymer layer, which could effectively fill the defect area and increase the compatibility with resins. The functionalized CF surface micromechanism was studied by TEM, as shown in Figs. 2(d)–2(f), the pristine CF surface (Fig. 2d) was very smooth, and no depression or protrusion was observed. After grafting GO (Fig. 2e), the transparent domains with a thickness of 208 nm could be observed on the CF surface, which increased the fiber surface roughness. For CF-GO-PA (Fig. 2f), the thickness increased to 836 nm, GO and PA could form hierarchical structure with gradient modulus, which could not only increase the chemical bond and mechanical interlocking between CF and epoxy, but also effectively balance and buffer modulus between fiber and matrix.

**Surface Chemical Compositions and Structure Composition of Functionalized CF**

The elemental compositions of pristine CF, CF-GO, CF-GO-PA were detected by recording the XPS, and the results were summarized in Table 1. The pristine CF surface was mainly composed of C, O and a small number of N elements. After grafting with GO, the C elements content decreased and O elements content increased sharply, and the O/C value increased sharply from 4.79% to 17.13%, which manifested that GO was grafted onto CF surface by esterification reaction. While the N element content of CF-GO-PA increased from 1.5% to 3.44% and the N/C value increased from 1.78% to 4.18%, which suggested that PA was successfully grown onto the CF-GO surface via caprolactam anionic polymerization.

C1s curve fitting spectra with different functionalized CFs were measured to investigate the chemical compositions, as shown in Fig. 3. The spectra (Fig. 3a) showed three distinct C1s, N1s, and O1s signals around 284.6, 400.5 and 523.1 eV, respectively. Theoretically, the C1s peaks of pristine CF (Fig. 3b) were deconvoluted and could be decomposed into three constituent peaks associated with the C sp² and C sp³ in the fiber of graphitic structure (284.4 eV), C—C bonding of amorphous carbon (285.6 eV) and C—O bond (286.3 eV). After being modified with GO, the C1s spectrum (Fig. 3c) showed extra binding energy peaks at 288.4 eV, which was attributed to —COOH generated by the esterification reaction on the CF-OH surface. The esterification reaction between CF and GO was verified by tracing O1s, and it was found that an additional peak (Fig. 3d) was generated at 532.3 eV, which derived from carbonyl oxygen atoms C—O—C—O in ester groups, indicating that GO was successfully grafted onto CF surface. For CF-GO-PA (Fig. 3e), the C1s spectrum produced two extra peaks at 285.3 eV and 287.9 eV, which were attributed to a new bond (C—N) produced by the primary amino groups and a new bond (O═C—N) produced between acyl chloride groups and primary amino groups of caprolactam monomer.[25] In addition, the deconvolution of the N1s peak of CF-GO-PA (Fig. 3f) produced C—N and O═C—N at 399.3 and 400.1 eV,[26] respectively. All the above XPS results further verified that the chemical bonds were constituted among CF, GO and PA via esterification and anion polymerization reactions.

The TGA curve of CF, CF-GO, CF-GO-PA were shown in
Fig. 4. Pristine CF showed extremely high thermal stability with char residues of 99.10% at 700 °C. The residual weight of CF-GO was 98.26%, which was attributed to the decomposition of oxygen-containing functional groups and covalent bonds (C–O–C=O) on the CF-GO surface, and the grafting amount was 0.84%. While the residual weight of CF-GO-PA was 97.50%, which indicated that PA has been successfully polymerized onto the CF-GO surface with a grafting amount of 0.76%.

**Surface Energy of Functionalized CF**

The contact angles of functionalized CFs in two testing liquids and surface free energies (including dispersion and polar components) were calculated to evaluate the wettability of the fiber with resin, as summarized in Fig. 5. A significant downward trend in contact angles of both polar water and nonpolar diiodomethane was detected for CF-GO and CF-GO-PA.

### Table 1  Surface chemical elements and groups of functionalized CFs

| Samples   | Atomic element content (%) | C  | N  | O  | O/C | N/C |
|-----------|-----------------------------|----|----|----|-----|-----|
| CF        |                             | 93.71 | 1.8 | 4.49 | 4.79 | 1.92 |
| CF-GO     |                             | 84.09 | 1.5 | 14.41 | 17.13 | 1.78 |
| CF-GO-PA  |                             | 82.15 | 3.44 | 14.41 | 17.54 | 4.18 |

Fig. 3  Wide-scan XPS spectra (a), C1s high-resolution XPS spectra of (b) CF, (c) CF-GO and (e) CF-GO-PA; (d) O1s high-resolution XPS spectra of CF-GO; (f) N1s high-resolution XPS spectra of CF-GO-PA.
Accordingly, the dispersive component, polar component and the surface free energy of CF-GO and CF-GO-PA were all significantly improved, which might be ascribed to the introduction of abundant amide groups of PA and epoxide groups of GO sheets and the increased surface roughness caused by plentiful wrinkled textures of GO and flexible PA chains. The increased surface energy would effectively facilitate the impregnation of resin on the CF surface and was beneficial to increase the interface performance of composites.

**Interface Phase Element Analysis**

To verify the existence of the gradient interface layer, EDS linear scanning system of SEM was adopted to evaluate the distribution of carbon element in interface area, as depicted in Fig. 6. For pristine CF/epoxy composite (Figs. 6a and 6d), a sudden drop in the content of carbon element could be
observed from CF to matrix. However, this down tendency became slower after grafting GO (Figs. 6b and 6e), and the thickness of interface phase increased to 0.75 μm, which indicated the formation of interfacial layer reinforced by GO in the CF/epoxy. For CF-GO-PA (Figs. 6c and 6f), the amount of carbon element lessened more relaxedly from CF to matrix, which manifested the gradient distribution of GO and PA in interfacial layer and supported the construction of multiscale gradient interface layers with a thickness of 0.96 μm. The gradient modulus intermediate layer would be beneficial to stress evenly transferring from epoxy resin to CF, thereby improving the interface properties of composites.

**Interfacial Performance of Functionalized CF/Epoxy Composites**

Fig. 7(a) shows the IFSS and ILSS results of epoxy composites reinforced with functionalized CF. The IFSS and ILSS values of CF-GO/epoxy composites increased from 48.8 and 58.6 MPa for pristine CF/epoxy composites to 78.5 and 76.9 MPa, which could be ascribed to the abundant active groups and larger specific surface area of GO surface. The CF-GO-PA/epoxy composites had the highest interfacial strength, the IFSS and ILSS reached 86.3 and 85.8 MPa, with the increasing amplitude of 76.8% and 46.4%, respectively. The improvement of interfacial performance could be ascribed to the following aspects. (1) As depicted in Fig. 7(b), the amino groups in PA and the remained hydroxyl groups on the CF surface would participate in curing and form a network structure with epoxy resin. (2) The grafting of GO and PA further increased the specific surface area of fiber, the adequate branched structures and holes in CF/epoxy interface regions could serve as anchors to increase the mechanical interlocking points with epoxy matrix. (3) GO and PA introduced a large number of oxygen-containing functional groups and amide groups on the CF surface, which greatly improved the surface free energy and wettability of the CF. (4) The GO and PA layer could promote the formation of a hierarchically structure intermediate phase with a multiscale gradient modulus between CF and epoxy, thereby reducing internal and external stress concentration. Hence, the IFSS and ILSS of CF-GO-PA/epoxy composites observably improved.

Ma et al.[19] used HDI tripolymer as the coupling agents to graft GO onto the CF surface, and the IFSS of CFO-NCO-g-GO/PA composite increased by 27.6%. Yuan et al.[28] adopted APTES as coupling agent to pretreat CF fabrics and then GO was deposited by EPD process on CF surface. The ILSS was improved by 37.3%. The above results signified that the architecture of multistage gradient modulus intermediate layer with rigid component GO and flexible chain PA was promising and rivalrous to prominently boost the interfacial performance of the CF composite.

In order to further understand the interface behaviors between the functionalized CF and matrix, the ILSS fracture surfaces of functionalized CF/epoxy composites were observed by SEM, and the various failure models were depended on the interfacial states,[29] as depicted in Fig. 8. The fractured surface of pristine CF composite was smooth and almost no matrix remained (Figs. 8a and 8d), which indicated the weak interface strength between CF and matrix. The failure mode was almost adhesive failure, as presented in Fig. 8(g). After GO grafting, the number of fibers pulled out reduced and some resin particles attached onto the CF surface (Figs. 8b and 8e), which manifested that the interface between CF-GO and matrix became stronger and the failure was not restricted to the interface only, the microscopic failure model was incorporation of adhesion and cohesive failure as shown in Fig. 8(h). For CF-GO-PA/epoxy composites, there were no interfacial peeling, holes and debonding

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**Fig. 7** (a) IFSS and ILSS of CF/epoxy composites and (b) schematic diagram of interface region.

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between CF and resin (Figs. 8c, 8f and 8i), and a layer of remained matrix on the CF surface could testify that the interfacial failure might transfer to dominant cohesive mode and occur in matrix.

**Mechanical Performances of Functionalized CF/Epoxy composites**

Compressive tests were adopted to further research the effect of hierarchically structure intermediate phase on compressive performances of CF composites. Fig. 9(a) showed the compressive load-displacement curves of the functionalized CF composites, indicating that the yield strength and strain varied simultaneously due to the collaborative hardening of the rigid GO-flexible chain PA. As the external load increased, the curves would produce yield point (maximum stress of the specimen). Fig. 9(b) showed compressive strength and modulus of the composites. Compared with pristine CF/epoxy composites, CF-GO-PA/epoxy composites show the highest compressive strength (956.6 MPa) and compressive modulus (195.2 MPa), with an increase of 40.7% and 14.4%, respectively, which could be attributed to the fact that rigid GO and flexible PA in interface region formed a mutually-supporting system. When the crack encountered rigid GO and flexible PA, more cracks could be induced and more fracture energy was absorbed effectively, thus improving the compression performance of composites.

In addition, as presented in Fig. 9(c), the impact toughness of CF/epoxy composites was performed to assess the damage resistance. The impact toughness of pristine CF and CF-GO composites was 55.7 and 69.3 kJ·m⁻², respectively. Nevertheless, the impact toughness of CF-GO-PA composite increased to 76.8 kJ·m⁻² after the establishment of rigid-flexible hierarchical structure, with an increase of 37.8% compared with pristine CF composite. The great improvement in impact toughness was connected with the interphase containing rigid GO and flexible polymer PA. We introduced one-dimensional CNTs and PA to construct double “rigid-flexible” structure with different sizes on the CF surface, and the im-

![Fig. 8](https://example.com/fig8.png)

**Fig. 8** The failure morphologies of fracture surfaces (a, b, c), laminates cross section (d, e, f) of functionalized CF composites and schematic diagrams of interface failure (g, h, i).

![Fig. 9](https://example.com/fig9.png)

**Fig. 9** (a) Stress-strain curves of compression, (b) compression strength and modulus and (c) impact properties of CF composites.
pact toughness of CF-CNTs-PA$_2$/epoxy composites increased by 34.6%.[17] In this study, the specific surface area and active functional groups of two-dimensional GO were much higher than those of CNTs, therefore, anionic polymerized PA could form a thicker multistage gradient modulus layer, which could exert stronger mechanical interlocking and chemical bonding. The thicker multistage gradient modulus intermediate layer could not only deliver load and absorb fracture energy, but also prevent physical damage caused by crack propagation.[18] Therefore, CF-GO-PA/epoxy composite exhibited an excellent damage resistance than other analogous composites.

CONCLUSIONS

In this work, an effective and alternative method for modifying the interfacial strength of CF composites was proposed by grafting of rigid GO nanosheets and flexible multifunctional polymer PA to construct multistage gradient modulus intermediate layer. The active groups, roughness, surface energy of CF-GO-PA surface and the thickness of intermediate layer were improved obviously. The IFSS, ILSS, compression strength and impact toughness of CF-GO-PA/epoxy composites increased by 76.8%, 46.4%, 40.7% and 37.8%, respectively. These results indicated that this rigid-flexible intermediate structure with multistage gradient modulus could achieve superior mechanical enhancement than other previous reports. Moreover, the intermediate layer could be regulated by varying PA polymerization time, and the design strategy could be extended to other system to cater different application fields.

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