Effect of Graphene on Graphitization, Electrical and Mechanical Properties of Epoxy Resin Carbon Foam

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Abstract: Epoxy resin (EP CF) carbon foam is a new carbon material with a three-dimensional sponge-like structure. The EP CF has high porosity, high temperature resistance, corrosion resistance, and adjustable electrical/thermal conductivity, which possesses broad application prospects. However, epoxy resin is difficult to graphitize. Therefore, graphene was used as a heterogeneous nucleation modifier to improve the graphitization degree, electrical conductivity and mechanical properties of EP CF. Graphene modified EP CF was prepared by a simple process of foaming, carbonizing, and graphitizing. Graphene as heterogeneous nucleation agent induce the carbon crystallite growth in EP CF, which increases the lattice fringe length and reduces carbon crystal tangled. The results show that the interplanar spacing (d_{002}), grain stacking height (L_c) and graphitization degree (g) of 0 and 0.05% (in mass) graphene modified EP CF are 0.343 nm, 3.35 nm and 8.42%, 0.342 nm, 10.22 nm and 23.2%, respectively. In addition, graphene as a nucleation site affects the average cell size of EP CF. With the increase of graphene content, the average cell size of EP CF decreases firstly and then increases. Meanwhile, graphene increases the ordered structure of EP CF and improves its conductivity. When graphene is 0.05% (in mass), the conductivity of EP CF is 53.8 S·m^{-1}. Compared with pure EP CF (compressive strain of 0.0096%), the compressive strains of 0.01%, 0.02%, 0.05%, and 0.1% (in mass) graphene modified EP CF increases to 0.208%, 0.228%, 0.187%, and 0.1146%, respectively. This study provides new research method for the preparation, carbon structure control, and properties of carbon nanomaterial/carbon foam.

Key words: carbon foam; graphene; heterogeneous nucleation; graphitization; mechanical property

Carbon foam is a typical porous material with superior properties, such as low density, high porosity, high temperature tolerance and excellent corrosion resistance[1], which can be applied in aeronautics, astronautics, chemicals, energy, environmental protection, and catalysis[2-4]. The precursors of carbon foam include pitch, resin, coal or biomass[5]. Epoxy resin carbons have the advantages of high strength, high temperature resistance, corrosion resistance, and permeability resistance, *etc*., which can be applied in high temperature carbon composite, energy storage electrode, carbon foam materials, *etc*[6-9]. However, the research and application of carbon foam from epoxy resin (noted as EP CF) are greatly restricted by the low char yield of epoxy resin, and non-graphitization, poor

mechanical strength and electrical conductivity[10]. Therefore, it is urgent to solve above problems of EP CF.

The preparation methods of carbon foam include template-assisted, foaming, direct pyrolysis, high temperature and high-pressure methods, *etc*[11-12]. Among these preparation methods, high temperature combined high pressure method demonstrated the advantages for tailoring the density and cell structure of carbon foam[13]. The increase of the graphitization degree of resin carbon materials can be divided into catalytic graphitization, carbon nanomaterial modified graphitization, and easy graphitization precursor modified graphitization. Compared with others, catalytic graphitization can decrease the graphitization temperature and reduce energy consumption.

However, the residual catalyst in resin carbon will substantially affect the properties of carbon foam. The easy graphitization precursor modified method can improve the graphitization degree and char yield. While there may occur phase separation between easy graphitization precursor and epoxy resin, and it is difficult to prepare homogeneous carbon materials[14-15]. In recent years, many studies of carbon nanomaterials (graphene, carbon nanotube and their derivative) have been developed. Graphene has excellent thermal, mechanical and electrical properties. Therefore, graphene is considered to be a very promising carbon nanomaterial for the modification of resin precursors. As SP2 carbon material, graphene can form π–π conjugation with the aromatic ring of epoxy resin, which can promote the arrangement and stacking of resin with the graphene plane. Thus it can be expected to improve the graphitization degree and electrical conductivity of resin carbon[16-17]. In addition, graphene has excellent mechanical properties, which can be employed as a reinforcement for improving the mechanical properties of EP CF.

In this work, graphene modified EP CF was firstly prepared *via* heating mixing at 100 ℃ for 0.5 h with a combination of high temperature and high pressure foaming method. The structure and property of the modified EP CF were characterized by X-ray diffraction (XRD), Raman spectroscope, scanning electron microscope (SEM), high-resolution transmission electron microscope (HRTEM), digital resistance meter and electronic universal testing machine. Moreover, the study also explored the effect of graphene on the graphitization degree, electrical conductivity and compression strength of EP CF.

1 Experimental

1.1 Materials and reagents

Graphene was obtained from Northwestern Polytechnical University of Shanxi Engineering Laboratory for Graphene New Carbon Materials and Applications. The density, thickness of graphene are 0.02–0.1 g·cm^{-3} and 10–15 nm, respectively (Fig. S1). Epoxy resin E44 was purchased from Xi'an Resin Factory, China, with an epoxy equivalent of 210–240 and softening point temperature of 15–23 ℃. Dichloromethane was purchased from Chemical Reagent Co., Ltd (≥99.5%).

1.2 Material preparation

Typically, dichloromethane solvent was used for the mixing of epoxy resin and different content of graphene (0, 0.01%, 0.02%, 0.05%, and 0.10%, in mass). Subsequently, the mixture was put in 25 mL ceramic crucible at 100 ℃ for 0.5 h, and then foaming at 450 ℃ and 2 MPa for 3 h . Then, the obtained products were carbonized at 1000 ℃ for 3 h, and graphitized at 3000 ℃ for 0.5 h to prepare EP CF (Fig. S2(a)). In order to determine the foaming temperature, the thermogravimetric curves of epoxy resin were tested. The 60% thermal weight loss is happened in the range of 400–450 ℃. As a result, 450 ℃ was selected as the foaming temperature (Fig. S2(b)). The foaming process was shown in Fig. S2(c).

1.3 Material characterization

The phase structures of EP CF were analyzed by X-ray diffractometer (XRD, D/Max 2500 V·PC^{-1}, Cu-Kα radiation). 10% (in mass) silicon powder was used as a marker, and the scanning rate was 5 (°)/min. The graphite interplanar distance (d_{002}), grain stacking height (L_c) and graphitization degree (g) were calculated by Bragg, Scherrer and Mering-Maire formula, respectively. The graphite structures of EP CF were studied by Raman spectroscope (Alpha 300R) with a 532 nm laser irradiation. The morphology and microstructure of the EP CF were observed by tungsten filament scanning electron microscope (VEGA3 LMU) and high-resolution transmission electron microscope (HRTEM, JEM 2100F), respectively. Thermogravimetric analysis of epoxy resin was carried out by STA449F3 thermal analyzer (Naichi, Germany), and the temperature was raised to 700 ℃ at 10 ℃·min^{-1} in the Ar. The electrical conductivity of EP CF was obtained by digital resistance meter. The compressive strengths of EP CF were analyzed by electronic universal testing machine. The sample size is 10 mm× 10 mm×10 mm, and the loading rate is 0.5 mm·min^{-1}. The electrical conductivity and compressive strengths of EP CF were the average value of three tests.

2 Results and discussion

2.1 XRD and Raman analyses

Fig. 1(a) is the XRD patterns of EP CF after graphitization at 3000 ℃ for 0.5 h. The diffraction peak of (002) crystal plane of crystalline graphite is near $2\theta=26°$. When the graphene content is 0.02% (in mass), the angle of (002) crystal plane diffraction peak is relatively small. The angle of (002) crystal plane diffraction peak of EP CF modified by 0.05% (in mass) graphene reaches the maximum ($2\theta=26.27°$). While the angle of (002) crystal plane diffraction peak of EP CF modified by 0.10% (in mass) graphene is smaller than the 0.05% (in mass) graphene modified EP CF. It indicates that the high graphene content could aggregate in the epoxy resin, and thus hinder the graphite crystallite growth. The microcrystalline parameters of modified EP CF
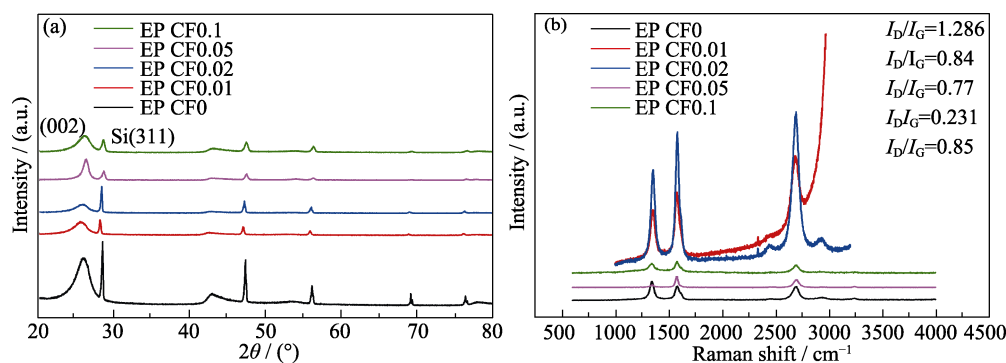
Fig. 1　Structure parameters of EP CF modified by different contents of graphene after graphitization treatment at 3000 ℃ for 0.5 h

(a) XRD patterns; (b) Raman spectra. Colorful figures are available on website

after graphitization at 3000 ℃ for 0.5 h are shown in Table S1. As shown in Table S1, the d_{002}, L_c and graphitization degree (*g*) of EP CF0 are 0.343 nm, 3.35 nm and 8.42%, respectively. While the d_{002}, L_c and *g* of EP CF0.05 were 0.342 nm, 10.22 nm and 23.2%, respectively. The graphitization degree of graphene modified EP CF is obviously increased by proper graphene content modification. Fig. 1(b) shows the Raman spectra of EP CF. The band at 1590 cm^{-1} is the G (graphite) band that originates from the stretching mode of sp^2 hybridized orbitals of carbon–carbon bonds. The band at 1350 cm^{-1} is attributed to D (disorder) band, which is the breathing mode of sp^2 hybridized carbon. The intensity ratio of the G to D band increases with the increase of graphene content, indicating that the proper graphene content can induce the graphite carbon growth of modified EP CF. I_D/I_G values of EP CF0 and EP CF0.05 is 1.286 and 0.231, respectively. The 2D peaks at 2700 cm^{-1} in all modified EP CF are observed, which show that the modified EP CF is turbostratic graphite and relative high degree of stacking[18-19]. Based on the XRD and Raman results, the proper graphene content can induce the graphite crystal growth and improve the graphitization degree, which can be helpful for improving the electrical conductivity and mechanical properties of EP CF.

2.2　SEM and TEM analyses

Fig. 2 is the SEM images of modified EP CF by different graphene contents after graphitization treatment at 3000 ℃ for 0.5 h. All EP CF show 3D cell structures. With the increase of graphene content in the modified EP CF, the average cell size firstly decreases and then increases, and the cell shapes of all EP CF are round. The average cell sizes of EP CF0 and EP CF0.02 is 675 and 456 μm, respectively. However, the micropore numbers firstly increases and then decreases. The variation of average cell sizes and micropore numbers in EP CF could be substantially influenced by the heterogeneous nuclei of graphene and gas. But the excess graphene can

aggregate in the epoxy resin, and decrease its heterogeneous nuclei effect for cell structure of EP CF (Fig. 2, Fig. S3)[20].
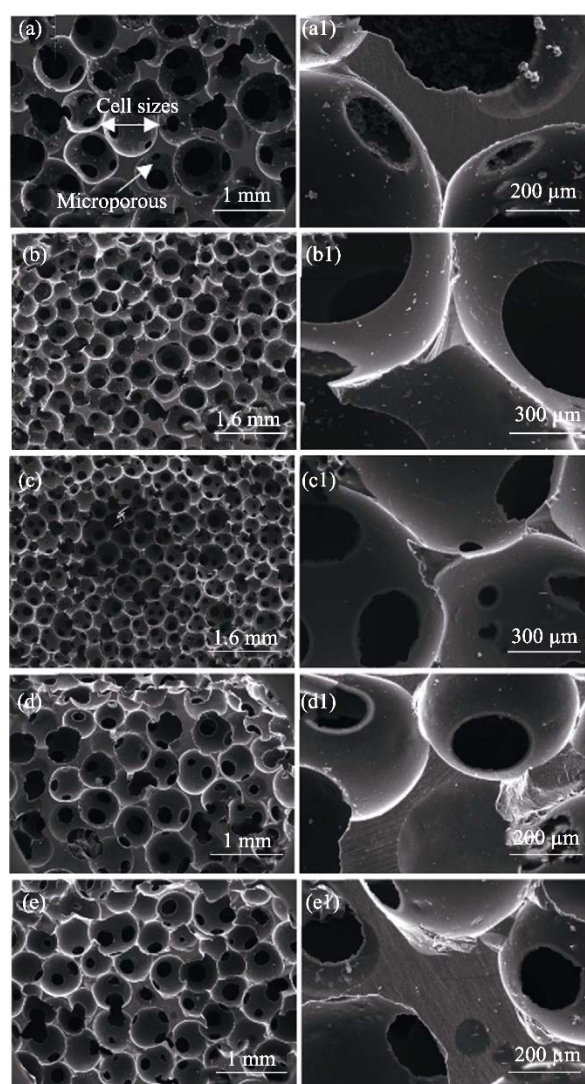

Fig. 2　SEM images of modified EP CF by different graphene contents after graphitization treatment at 3000 ℃ for 0.5 h

(a, a1) EP CF0; (b, b1) EP CF0.01; (c, c1) EP CF0.02; (d, d1) EP CF0.05; (e, e1) EP CF0.1
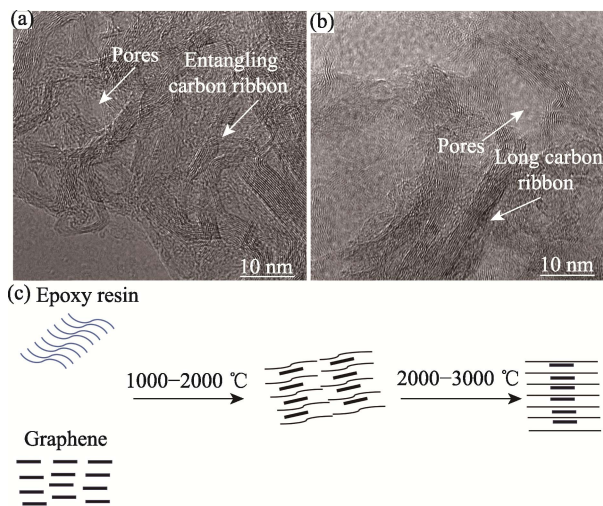
Fig. 3　HRTEM images of EP CF and its graphitization mechanism

(a) EP CF0; (b) EP CF0.05; (c) Schematic diagram of graphitization mechanism of EP CF treated at 3000 ℃ for 0.5 h

It is observed from Fig. 3 that the microcrystalline structures of EP CF0 and EP CF0.05 show obviously different. The EP CF exhibits microporous structure, entangled carbon ribbon and isotropic amorphous carbon, indicating EP CF with poor crystallinity (Fig. 3(a)). EP CF0.05 is less tangled microporous structure with longer lattice fringes and, demonstrating that the graphene can improve the ordered graphite carbon content of EP CF (Fig. 3(b)). The HRTEM result is consistent with the XRD and Raman analyses. The above carbon structure difference of EP CF can be explained from the epoxy resin molecular and graphene structure. The epoxy resin contains aromatic ring and the graphene is sp^2 carbon, which can produce the π–π interaction between them. The epoxy resin molecules are arranged and grown along the plane direction of graphene in the process of melting, carbonizing and graphitizing. In addition, the volume shrinkage of graphene is smaller during the carbonization and graphitization treatment, while the epoxy resin has a larger volume shrinkage during the carbonization and graphitization treatment process. The mismatch in the thermal expansion coefficient between them can increase the interfacial thermal stress, and promote the stress graphitization of EP CF (Fig. 3(c))[17].

2.3　Electrical conductivity

Electrical conductivity is an important property of carbon foam, which is used to characterize conductive ability of carbon foam. Fig. 4 and Table S2 presents the variation of electrical conductivity of modified EP CF with different contents of graphene at room temperature. It is observed that the electrical conductivity of the graphene modified EP CF firstly increases and then decreases with the graphene from 0 to 0.10% (in mass). EP CF0.05 can form a good electrical conductivity
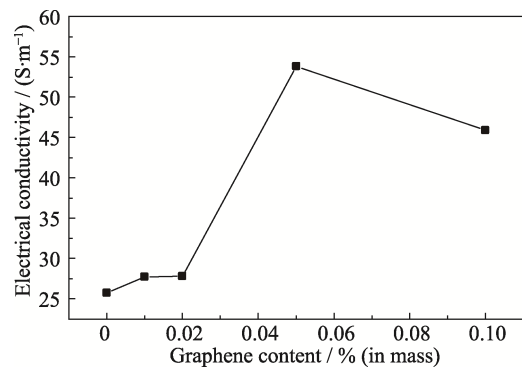

Fig. 4　Electrical conductivity of EP CF modified by different contents of graphene after treatment at 3000 ℃ for 0.5 h

network of carbon matrix[21]. The electrical conductivity of EP CF0 and EP CF0.05 is 25.79 and 53.8 S·m^{-1}, respectively. More graphene nanosheets in EP CF results in an increase in the crystallite growth of EP CF matrix. Thus it is beneficial to improve the electrical conductivity of the modified EP CF. In addition, the high electrical conductivity of graphene can contribute to the improvement of the electrical conductivity of EP CF. However, the electrical conductivity of the modified EP CF0.1 decreases. A possible reason is due to the aggregation of high graphene content, which hinders the carbon crystal growth and decreases the electrical conductivity of EP CF (Fig. 1, Fig. 3).

2.4　Compressive strength

The compressive strength of the graphene modified EP CF is shown in Fig. 5(a) and Table S2. The compressive strength of the graphene modified EP CF firstly increases and then decreases with an increase graphene content from 0 to 0.10% (in mass). The compressive strength of the EP CF0.01 and EP CF0.02 is 4.9 and 4.82 MPa, respectively. They are almost 1.5 fold of that of EP CF0. The improvement of the compressive strength could be related to the reinforcement effect from graphene, and reduce the crack elongation during the mechanical test. However, the compressive strength of the modified EP CF decreases when the graphene content increases to 0.10% (in mass) due to the aggregation of graphene content. It can significantly reduce the strength of EP CF. Fig. 5(b) shows typical stress-strain curves of the modified EP CF with different graphene contents. It is found that the three stages for the deformation mechanism of EP CF, such as elastic deformation, plastic deformation and final failure. The compressive strain of the EP CF0 is 0.0096%, whereas those of EP CF0.01, EP CF0.02, EP CF0.05 and EP CF0.1 are 0.208%, 0.228%, 0.187% and 0.1146%, respectively. The results indicate that graphene can toughening the EP CF and increase its failure strain. This can be originated from the micro-cracks and defects propagating *via* a deflection and blocking of graphene[22].
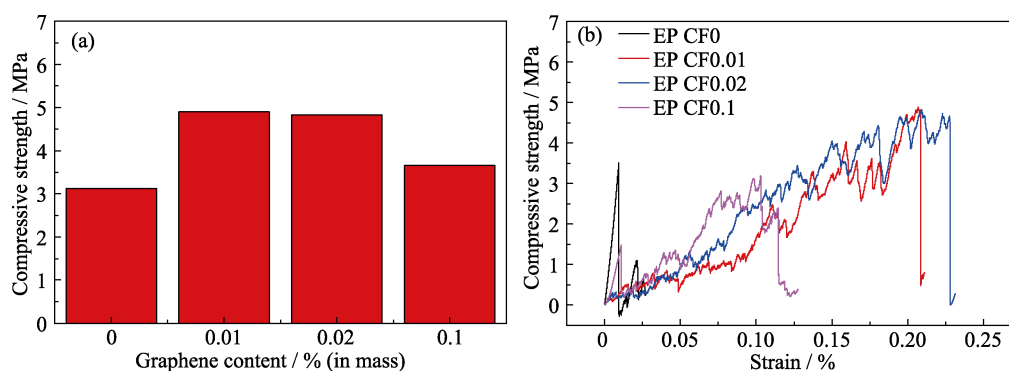
Fig. 5　Mechanical properties of EP CF modified by different graphene contents after graphitization at 3000 ℃ for 0.5 h
(a) Compressive strength; (b) Variation of stress with strain; Colorful figures are available on website

3　Conclusions

In this work, graphene modified EP CF was firstly prepared *via* a combination of high temperature and pressure, and graphitization methods. Results shows that the graphene can induce the crystal growth of EP CF, where the d_{002}, L_c and g of EP CF0.05 are optimized to 0.342 nm, 10.22 nm and 23.2% compared to EP CF0 (0.343 nm, 3.35 nm and 8.42%). In HRTEM images, the EP CF0.05 exhibits microporous structure, longer lattice fringes and less tangled carbon ribbon. The average cell sizes and micropore numbers of EP CF can be regulated by the variation of graphene contents. With the increase of graphene content in the modified EP CF, the average cell size firstly decreases and then increases. The average cell sizes of EP CF0 and EP CF0.02 are 675 and 456 μm, respectively. Furthermore, the carbon crystal growth, electrical conductivity of EP CF can be significantly improved by the addition of graphene. Especially, the electrical conductivity of the graphene modified EP CF increases from 25.79 to 53.8 S·m^{-1} when the content of graphene increasing from 0 to 0.05% (in mass). Lastly, mechanical performance of EP CF could also be augmented by the incorporation of graphene. The compressive strength of the EP CF0.01 and EP CF0.02 are 4.9 and 4.82 MPa respectively. They are about 1.5 fold of that of EP CF0. Meanwhile, the compressive strain of the EP CF0 is 0.0096%, whereas the EP CF0, EP CF0.01, EP CF0.02, EP CF0.02, EP CF0.05 and EP CF0.1 are increased to 0.208%, 0.228%, 0.187% and 0.1146%, respectively. This study provides a guidance for the preparation of high performances EP CF.

Supporting materials:

Supporting materials related to this article can be found at https://doi.org/10.15541/jim20230385.

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石墨烯对环氧树脂泡沫炭石墨化、电导率和力学性能的影响

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摘 要: 环氧树脂基泡沫炭是一种具有三维海绵状结构的新型炭材料, 独特的网状泡孔结构使其具有高孔隙率、耐高温、耐腐蚀、导电/导热可调等性能, 应用前景广阔。但是环氧树脂的石墨化困难, 本工作以石墨烯为异质成核改性剂, 用以提高环氧树脂泡沫炭的石墨化程度、电导率和力学性能。采用简单的发泡、炭化和石墨化工艺制备了石墨烯改性环氧树脂泡沫炭。石墨烯异质成核剂诱导了泡沫炭碳微晶生长, 增加了碳晶格条纹长度, 减少了碳晶体混乱。研究表明, 不含或含质量分数 0.05% 石墨烯改性泡沫炭的晶面间距、晶粒堆垛高度、石墨化度分别为 0.343 nm、3.35 nm、8.42% 和 0.342 nm、10.22 nm、23.2%。此外, 石墨烯作为晶胞成核位点会影响泡沫炭的平均晶胞尺寸, 随着石墨烯含量的增加, 泡沫炭平均晶胞尺寸先减小后增大。同时, 石墨烯改性增大了泡沫炭的有序结构, 提高了其导电性, 当石墨烯的质量分数为 0.05% 时, 泡沫炭电导率为 53.8 $S\cdot m^{-1}$。相对于纯泡沫炭(压缩应变为 0.0096%), 质量分数 0.01%、0.02%、0.05% 和 0.10% 的石墨烯改性泡沫炭压缩应变增加至 0.208%、0.228%、0.187% 和 0.1146%。本研究为碳纳米材料/泡沫炭制备、碳结构和性能调控提供了新的研究方法。

关 键 词: 泡沫炭; 石墨烯; 异质成核; 石墨化; 机械性能

Supporting Information:

Effect of Graphene on Graphitization, Electrical and Mechanical Properties of Epoxy Resin Carbon Foam

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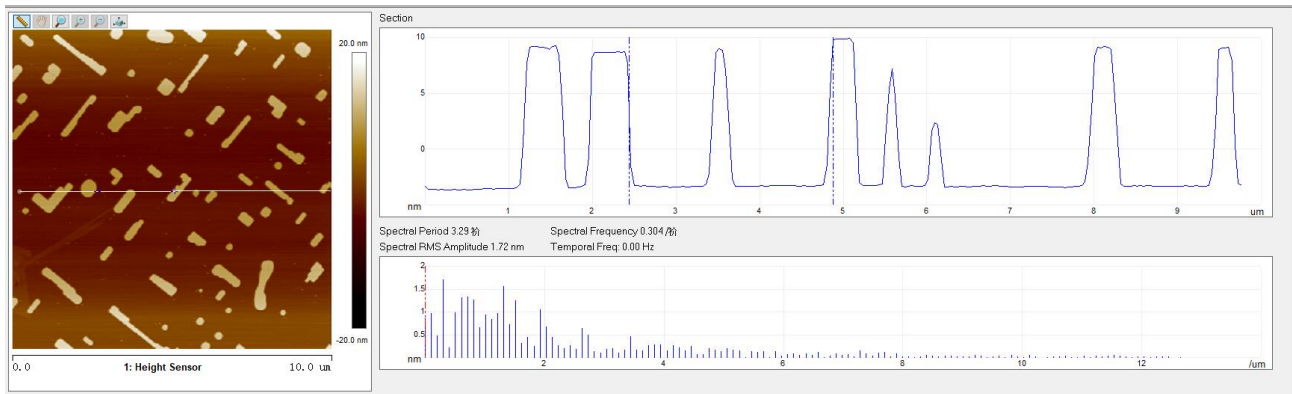
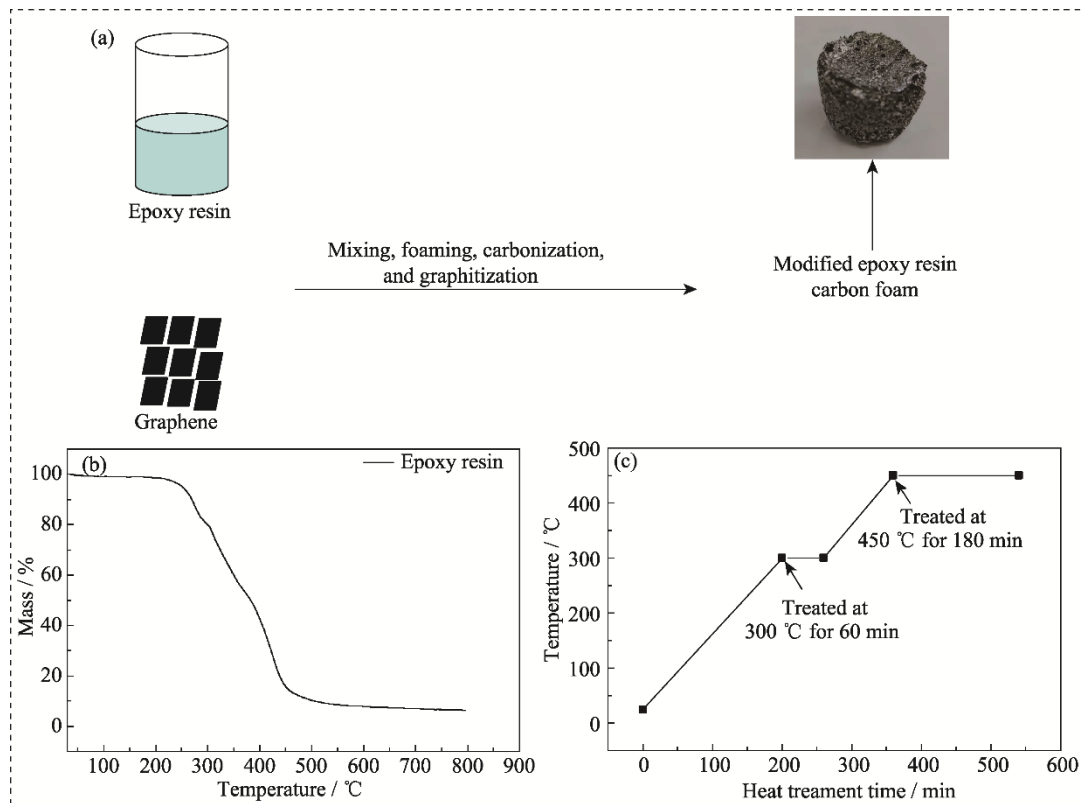Fig. S1   Graphene thickness analyzed by atomic force microscope

Fig. S2   (a) Preparation of graphene modified EP CF; (b) Thermogravimetric curve of epoxy resin; (c) Foaming temperature curve of green EP CF

Table S1   Crystalline parameters of EP CF modified by different graphene contents after treatment at 3000 ℃ for 0.5 h

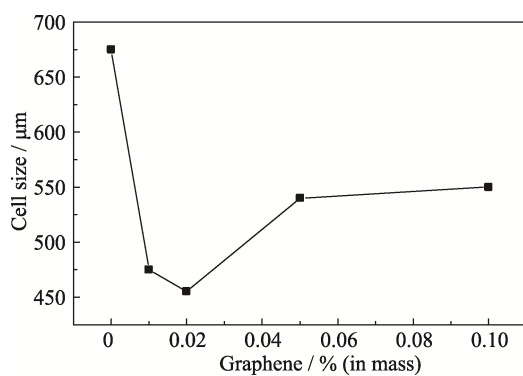| Sample	$2\theta_{002}$/(°)	d_{002}/nm	L_c/nm	g/%
EP CF0	25.9	0.3431	3.35	8.42
EP CF0.01	25.6	0.343	3.62	11.22
EP CF0.02	25.77	0.343	4.22	11.22
EP CF0.05	26.27	0.342	10.22	23.2
EP CF0.1	26.1	0.3425	4.46	16.5

Fig. S3   Cell sizes of different graphene contents modified EP CF prepared by graphitization treatment at 3000 ℃ for 0.5 h

Table S2 Physical, electrical and mechanical properties of EP CF modified by different graphene content after graphitization treatment at 3000 ℃ for 0.5 h

Sample	Density/(g·cm^{-3})	Electrical conductivity/(S·m^{-1})	Compressive strength/MPa
EP CF0	0.470	25.79	3.13
EP CF0.01	0.460	27.70	4.90
EP CF0.02	0.469	27.79	4.82
EP CF0.05	0.460	53.80	2.00
EP CF0.1	0.463	45.90	3.66