Influence of Extrusion Temperature on Property of Graphene Oxide-carbon Fiber Hybrid Reinforced Resin Matrix Composites

Yuqin Ma (yqma@xidian.edu.cn)
Xidian University https://orcid.org/0000-0002-5162-2198
Fei Li
Xidian University
Wei Xu
Xidian University
Long Yan
Xi'an University of Architecture and Technology
Haiyin Guo
Xidian University
Yatao Li
Xidian University
Mingtao Cui
Xidian University
Hao Jin
Xidian University

Original Article

Keywords: Vacuum Infiltration Hot-Pressing Molding Process, Graphene Oxide-Carbon Fiber, Hybrid Enhancement, Extrusion Temperature, Microstructure, Properties

Posted Date: May 13th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-482163/v1

Influence of extrusion temperature on property of graphene oxide-carbon fiber hybrid reinforced resin matrix composites

Yuqin Ma[1],*, Fei Li[1], Wei Xu[1], Long Yan[2],*, Haiyin Guo[1], Yatao Li[1], Mingtao Cui[1] and Hao Jin[1]

[1] School of Mechano-Electronic Engineering, Xidian University, Xi'an 710071, China; lifeili1123@163.com(F.L.); 396353159@qq.com(W.X.); haiyin_guo@163.com(H.G.); 23437323@qq.com(Y.L.); cuimt@mail.xidian.edu.cn(M.C.); jh2574846994@163.com(H.J.)

[2] School of Mechano-Electronic Engineering, Xi'an University of Architecture and Technology, Xi'an 710055, China；huanglong731@xauat.edu.cn(L.Y.)

* Correspondence: yqma@xidian.edu.cn(Y.M.); huanglong731@xauat.edu.cn(L.Y.)
Tel.:+86-29-8820-3115(Y.M.)

Abstract: The graphene oxide-carbon fiber hybrid reinforced resin matrix (GO-CF/EP) composites were prepared by vacuum infiltration hot-pressing molding process. The effects of extrusion temperature on the microstructure, fracture mechanism and mechanical properties of GO-CF/EP composites were investigated by setting different extrusion temperatures. In the experiments, the extrusion temperature was controlled as 30℃, 40℃, 50℃, 60℃ and 70℃ respectively. It was found that the best mechanical property of composites and infiltration effect of matrix in the fiber gap were obtained at the temperature of 50℃. The bending strength of the material reached 977 MPa through the performance test. The results showed the matrix viscosity was high and the fluidity was poor when the extrusion temperature was low. Poor penetration of the matrix resulted in a large number of fibers failing to bond together. The stress was difficult to transfer to other fibers through the matrix and the strengthening effect of graphene oxide (GO) was weak when the composite was subjected to external force. This phenomenon led to poor mechanical properties of composites. Under the condition of higher temperature, the flow speed of the matrix and the curing speed of composites could be improved. As a result, some of the matrix was solidified in advance while being pressed out, which led to cracks and other defects in the process of loading and affects the

mechanical properties of the composites. However, the mechanical properties of the composites with higher extrusion temperature were better than those with lower extrusion temperature due to the existence of graphene oxide in the fiber gap.

Keywords: Vacuum Infiltration Hot-Pressing Molding Process; Graphene Oxide-Carbon Fiber; Hybrid Enhancement; Extrusion Temperature; Microstructure; Properties

1. Introduction

Graphene oxide-carbon fiber hybrid reinforced resin matrix composite is a new type of composite material with nano-graphene oxide added into CFRP. GO is widely used to enhance the performance of composites due to its excellent mechanical, electrochemical and thermal properties. The composites with GO not only have significant improvement in mechanical properties, but also have obvious advantages in optical, thermal and shielding properties.[1] GO is a two-dimensional intermediate formed by exfoliation of original graphene during oxidation.[6] GO is used as a reinforcing phase of the composites, because GO has better dispersion stability in solution than original graphene.[7] At present, researchers mainly use mechanical dispersion, ultrasonic dispersion and microwave radiation to obtain GO dispersion. GO is dispersed in organic solvent, and it can be peeled into single sheet structure after ultrasonic treatment. This is conducive to the uniform dispersion of GO in the solvent, and the ability of uniform dispersion in the matrix is significantly improved.[8] In addition, some chemical functional groups on the surface of GO are combined with the matrix, which makes the two fully contact. This contact enhances the ability of the composites to transfer load. In this study, GO dispersion was prepared by ultrasonic dispersion method and GO-CF/EP composites were prepared by vacuum infiltration hot-pressing molding process. Extrusion molding can timely exhaust the gas among the fibers and make the solidified mixed solution fully infiltrate the fiber gap, so as to reduce the shrinkage cavity, porosity and other defects of the composites. It can also improve the density and bearing capacity of the composites.[9] In order to obtain the composites with compact structure and good mechanical properties, the parameters should be strictly controlled in the forming process. The extrusion temperature is an important parameter in the hot-pressing process. Its selection is directly related to the properties of the composites. If the extrusion temperature is too low, the flow velocity of the matrix will be affected and the effect of the matrix infiltration reinforcement will be poor. If the extrusion temperature is too high, the solidification speed of the matrix will be too fast to form a good matching relationship between the solidification speed and the flow speed. The matrix is not fully infiltrated into the fiber gap and the curing behavior occurs first, which affects the mechanical properties of the composites.[10] Therefore, it is the key to select the appropriate temperature to extrude the composites to prepare GO-CF/EP composites with excellent mechanical properties by vacuum infiltration hot-pressing molding process.

At present, researchers at home and abroad have carried out a large number of experiments and studies on the influence of extrusion temperature on composite materials. Fard et al.[11] studied the effects of extrusion temperature on the microstructure and porosity of A356-SiC_p composites. It was found that the grain refinement of SiC_p decreased first and then increased with the increase of extrusion temperature, while the porosity of the composites decreased. Wang et al.[12] obtained the variation of tensile strength of SiCp/Mg-Zn-Ca composites with extrusion temperature. It was found that the grain refinement of SiCp varies with extrusion temperature. Shao et al.[13] prepared graphene nano sheet reinforced Al6061 composites by pressure infiltration method, and studied the influence of extrusion temperature on the composites. The results showed that the deformation behavior and dispersion of graphene were different due to different extrusion temperature. Ma et al.[14] prepared 2D-C_f/Al composites by liquid extrusion and infiltration method, and studied the effects of extrusion temperature on the microstructure and mechanical properties of composites. However, there are few studies on the influence of extrusion temperature on GO-CF/EP composites. Therefore, the influence of process parameters on GO-CF/EP composites need to be solved urgently.

In order to explore the effects of extrusion temperature on the microstructure mechanism and mechanical properties of GO-CF/EP composites, the vacuum infiltration hot-pressing method was adopted in this study. Based on the analysis of the properties and forming characteristics of matrix and reinforcement, the experiment was carried out. During the experiment, DNS100 electronic universal testing machine was used to test the three-point bending properties of the composites, and the internal microstructure and bending fracture section morphology of the composites after impregnation were observed by JEOL JSM-6390A scanning electron microscope. The influence of extrusion temperature on the composites during the preparation of GO-CF/EP composites was analyzed and summarized. The experimental results will lay a theoretical and experimental foundation for the later preparation and further study of GO-CF/EP composites.

2. Vacuum infiltration hot-pressing experimental system and preparation method of composites

2.1 Vacuum infiltration hot-pressing experimental system

In this study, GO-CF/EP composites are prepared by vacuum infiltration hot-pressing molding process. The experimental system is consisted of four parts. They are fiber pre-forming module, vacuum heating infiltration module, hot-press curing molding module and data acquisition control module.[15] The fiber pre-forming module mainly includes fiber cloth cutting device, solid solution stirring device and ultrasonic dispersion device, etc. The system can make the solution preliminarily impregnation into the fiber cloth lamination and fiber gap to obtain the carbon fiber preform. The vacuum heating infiltration module mainly includes vacuum heating drying oven and vacuum pump, etc. The purpose of heating and drying is to promote the fluidity of the solution under high temperature conditions. The vacuum environment can make the composites discharge excess gas, which is conducive to the full impregnation of the solution in the fiber. The surface of the composites solidifies after the vacuum impregnation, but the interior of the composites are still in a state of incomplete solidification. It needs to be completely solidified by hot extrusion at a certain temperature. The final processing of the composites is carried out by hot-press curing molding module, which mainly includes heating die, hydraulic press and other devices. The composites can not only have a certain thickness but also obtain the required mechanical properties after hot-pressing. Temperature sensor, pressure sensor, digital vacuum gauge and other controllers are used to convert non electrical signals into electrical signals and input them to the computer in the whole preparation system. The computer controls all the parameters in real time. When the parameters are abnormal, it can be adjusted in time to meet the production requirements. The composition of the whole system is shown in Figure 1.

2.2 Experimental materials and preparation of GO-CF/EP composites

2.2.1Materials

The GO used in this study is prepared by Shenzhen Suiheng Technology Co., Ltd using an improved Hummer process. Its sheet diameter is 0.2-10μm, the thickness is 1nm, the number of layers is 1-2 and the purity is 99%. The resin matrix and curing agent are E-51 epoxy resin and phenolic amine T31 curing agent produced by Nantong Star Synthetic Composite Material Co., Ltd. T700 unidirectional carbon fiber cloth is produced by Toray Co., Ltd. Its tensile strength is 3920MPa, the elongation is 1.71% and the bending strength is 754MPa. The ethanol solution with 99.7% concentration is produced by Jiangsu Qiangsheng Functional Chemistry Co., Ltd.

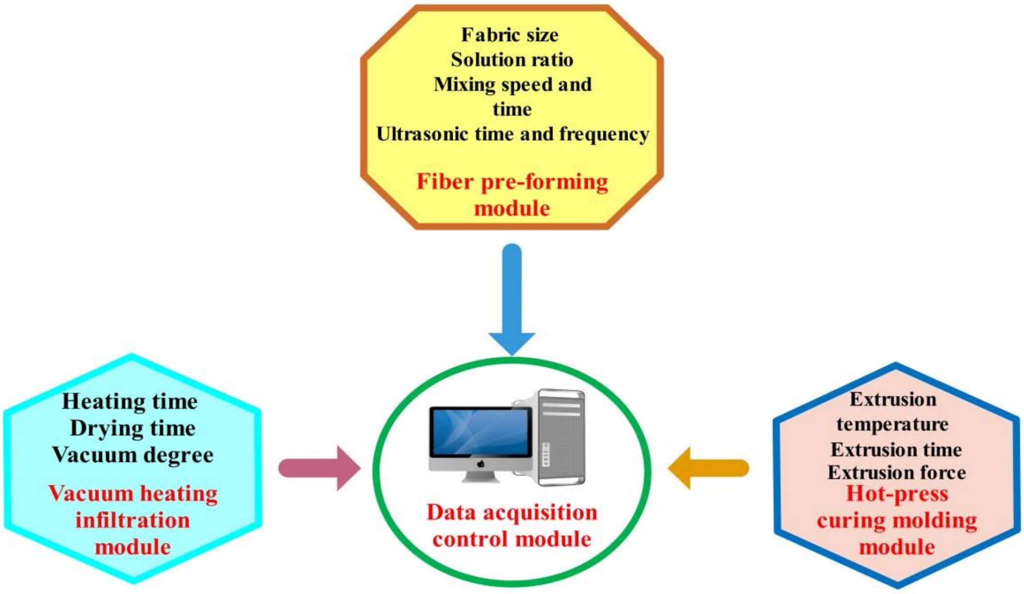

Figure 1. Vacuum infiltration hot-pressing experimental system

2.2.2 Preparation of GO dispersion

In general, the dispersion of GO in the matrix solution is poor due to the insolubility of GO in the matrix and the presence of some molecular forces between the matrix and GO. In order to improve the aggregation and precipitation of GO in the matrix of composite materials, ultrasonic dispersion of GO in ethanol solution is used in this paper. The specific dispersion process is carried out according to the following steps. Firstly, a certain amount of GO powder and anhydrous ethanol solution are weighed. The two are mixed and initially stirred manually. Secondly, the mixed solution is transferred to the electromagnetic stirring device, and the mixed solution is stirred for 20 minutes at a speed of 300rpm. Then the agitated solution is ultrasonically dispersed at 40kHz and 200W for 30 minutes. Finally, the suspension completed ultrasonic dispersion is placed in a vacuum pump to extract a vacuum for 6 to 8 hours to obtain GO dispersion. The preparation process of GO dispersion is shown in Figure 2.

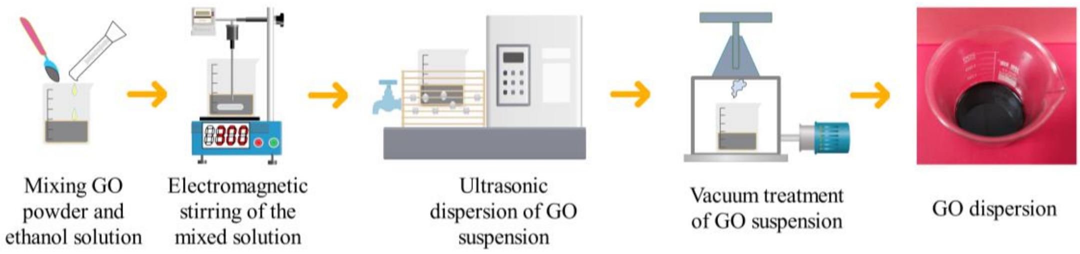

Figure 2. Preparation process of GO dispersion

2.2.3 Preparation process of GO-CF/EP composites

The preparation process of GO-CF/EP composite materials strictly follows the vacuum infiltration hot-pressing molding process, which is generally divided into four steps. 1) T700 carbon fiber cloth is cut for use. T31 curing agent and E-51 epoxy resin with mass ratio of 4:1 are added into the prepared GO dispersion to stir evenly to form a curing mixed solution. The prepared solution is placed in a vacuum pump for 6 to 8 hours to extract the internal alcohol to prevent the alcohol from oxidizing the resin. Finally, the solution is coated on both sides of each piece of fiber cloth, and placed in layers in turn. The initial compaction is carried out, and some bubbles in the inner part are discharged. The specimens are cured at room temperature for 4-6 hours. 2) The composites are placed in a vacuum drying oven with a vacuum degree of -0.09MPa and the temperature of 60°C to 100°C for 20 minutes. The high temperature condition is conducive to improving the fluidity of the solution and making the matrix fully permeate, and the vacuum environment can effectively prevent the occurrence of pores, bubbles and other defects. 3) The composite laminated materials are taken out and placed in the hot-pressing die preheated in advance, and the pressure is guaranteed to be 0.7MPa. The extrusion temperature is controlled to be 30°C, 40°C, 50°C, 60°C and 70°C successively, and the pressure is held for 1 hour. 4) The composites are taken out after the mold cools to room temperature when the hot-pressing process is stoppe. The process is shown in Figure 3.

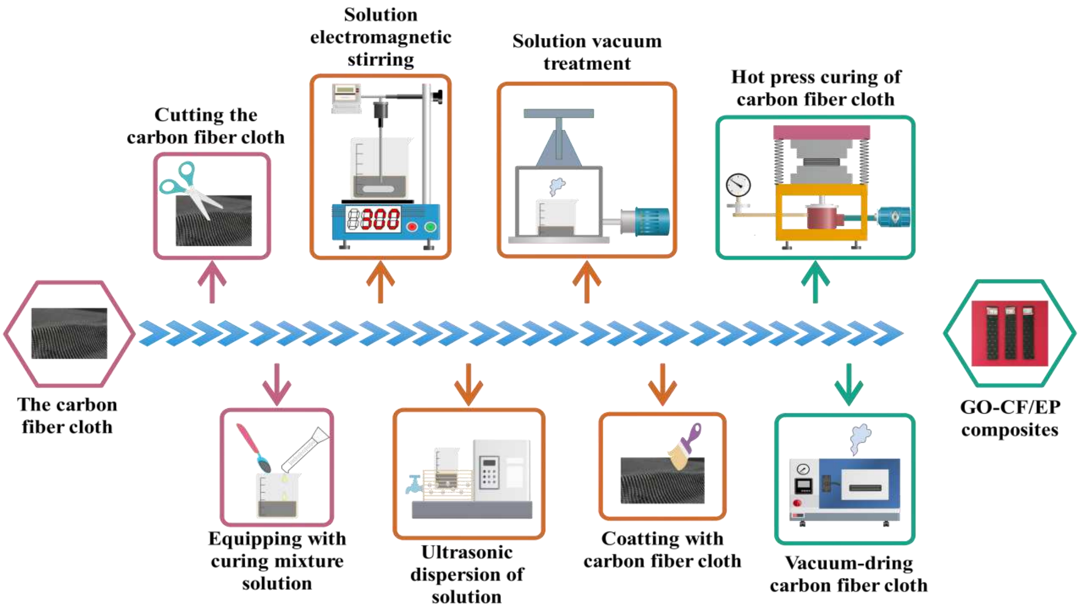

Figure 3. Preparation process of GO-CF/EP composites

3. Testing and characterization

The bending properties of GO-CF/EP composites at different extrusion temperatures were tested by three-point bending test according to GB/T3356-2014. The bending strength (σ_f) and bending modulus (E_k) of the specimen are calculated from equations (1), (2) and (3). The DNS100 electronic universal testing machine of Changchun machinery institute is adopted. The loading head and bearing radius are 5mm, the span thickness ratio is 32:1, the loading speed is 5mm/min, and the specimen size is 80mm×12.5mm×xmm. Thickness x is measured by the actual size of the specimen. The loading diagram is shown in Figures 4(a) and (b).

$$\sigma_{\mathrm{f}} = \frac{3P_{\max}L}{2\omega h^2} \tag{1}$$

$$\varepsilon_{\mathrm{f}} = \frac{6\delta h}{L^2} \tag{2}$$

$$E_{\mathrm{k}} = \frac{\Delta\sigma}{\Delta\varepsilon} \tag{3}$$

Where σ_f(MPa) is the bending strength of the specimen, P_{max}(N) is the maximum load of the sample, L(mm) is the span, H(mm) is the thickness of the sample, ω(mm) is the specimen width, ε_f(mm/mm) is the failure strain, δ(mm) is the deflection of the specimen in the middle of the span, E_k(GPa) is the bending modulus of the specimen, Δσ(MPa) is the difference of bending stress between two selected strain points, and Δε(mm/mm) is the difference of strain between two selected strain points.

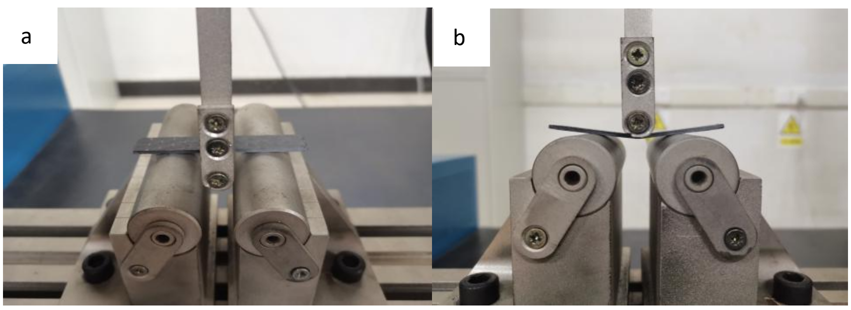

Figure 4. Loading diagram of three-point bending

4. Results and discussion

4.1 The bending property

The three-point bending tests are carried out on composites prepared at extrusion temperatures of 30ºC, 40ºC, 50ºC, 60ºC and 70ºC respectively. The load and displacement data in the test process are collected by the sensor on the test machine and sent to the computer. The collected experimental data are collated to get the test results as shown in Table 1.

According to the collected data, the load and displacement data of each group of specimens are plotted as shown in Figure 5. The load-displacement curve can directly reflect the relationship between the deformation and the load of the specimen in the process of loading.

Table 1 The bending test results.

Specimen Number	The Thickness of The Specimen/mm	Bending Strength/MPa	Bending Modulus/GPa
FC-1	1.64±0.14	513±18	96±4
FC-2	1.49±0.01	685±12	132±5
FC-3	1.52±0.06	977±14	142±6
FC-4	1.52±0.06	718±8	105±4
FC-5	2.18±0.08	760±9	81±3

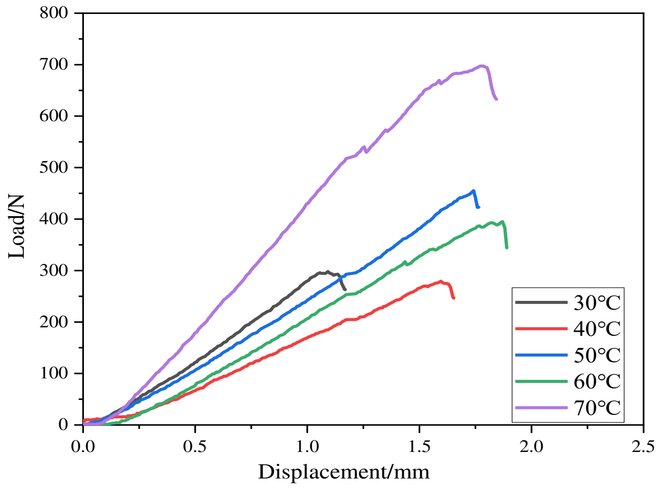

Figure 5. Load - displacement curves of composites at different extrusion temperatures

As shown in Figure 5, the loads of 5 groups of samples along with the increase of displacement are on the rise in the early stages of the loading phase. With the continuous increase of displacement and load, specimens under transverse cracks began to appear and the composite materials occur failure behavior when the load exceeds the limit load of the composite materials. Among the five groups of specimens, the thickness difference of specimens at extrusion temperature of 30°C, 40°C, 50°C and 60°C is within 0.3mm. The bending load of composites at extrusion temperature of 50°C is the largest, which can reach 455N. The specimens with extrusion temperature of 70°C can bear a large load due to the influence of the thickness of the composite materials. However, its bending strength and modulus are lower than those of the composites with extrusion temperature of 50°C.

Figure 6 shows the bending strength and the bending modulus of GO-CF/EP composites at different extrusion temperatures. With the increase of extrusion temperature, the bending strength of GO-CF/EP composites increases first and then decreases, and then increases slightly. The bending modulus increases first and then decreases. The maximum bending strength and bending modulus of the composites are 977MPa and 142GPa respectively when the extrusion temperature is 50°C. Compared with the extrusion temperature of 30°C, the bending strength and bending modulus are increased by 90.4% and 47.9% respectively. The cause of this change is that the viscosity and the liquidity of the matrix are greatly influenced by temperature. When the extrusion temperature is lower, the matrix has high viscosity and poor fluidity, which is mostly distributed among layers and the upper and lower surfaces of the composite materials. The stress on the fiber filaments is more concentrated, and GO is difficult to disperse the stress. The mechanical properties of the composite materials are poor. The matrix fully populated organization internal clearance due to its excellent liquidity and the fibers are tightly bound by the matrix in the gap with the rise of temperature. When an external force is applied, the bonded filaments share the stress and the GO dispersed within the fibers also contributes to some of the stress. This phenomenon effectively enhances the bearing capacity of composite materials, but the high extrusion temperature will increase the solidification rate and make the matrix partially squeezed out. Therefore, the mechanical properties of composites are reduced.

4.2 Influencing factors of resin viscosity

Epoxy resin is widely used in composite materials to bond reinforcers for its excellent properties such as high bond strength and plays a role in transferring stress, so as to the mechanical properties of the reinforcement are fully utilized. However, the temperature will directly affect the viscosity of matrix solution in the heating molding process of composite materials. The relationship between temperature and resin viscosity can be intuitively obtained from the double Arrhenius viscosity model in equation (4).[16]

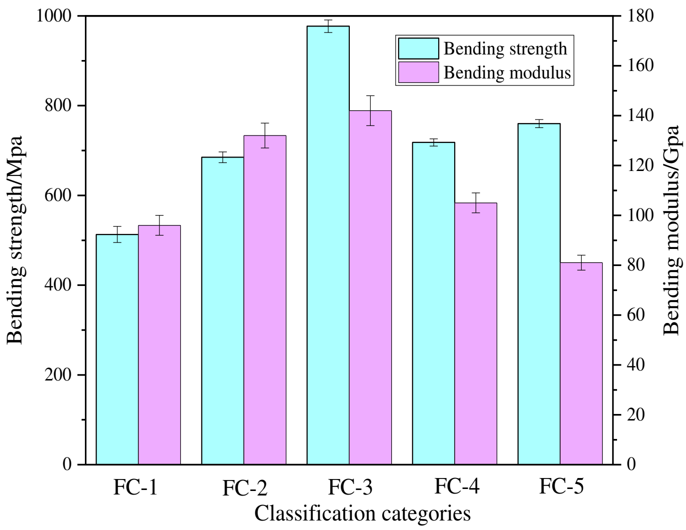

Figure 6. The bending strength and bending modulus of the composites at different extrusion temperatures

$$\ln \eta(T, \mathrm{t}) = \ln Z_{\infty} + \frac{E_Z}{RT} + K_0 e^{-\frac{E_T}{RT}} t \tag{4}$$

Where η is the viscosity of resin, Z_{∞} and K_0 are the Arrhenius pre-exponential factors, E_z is the activation energy of the solution flow, E_t is the activation energy of curing reaction, R is the gas molar constant, and T and t are reaction temperature and reaction time respectively.

According to equation 4, it can be intuitively obtained that the resin viscosity decreases with the increase of temperature. The gradual decrease of viscosity promotes the increase of resin fluidity, so that the matrix can be sufficiently immersed into the interior of the fiber bundle to bond the filaments. Therefore, the composite materials have a good bearing capacity. Although the rise of temperature helps to improve the liquidity of matrix, the viscosity of the resin will be affected after joining the GO nanoparticles. The higher the content of nanoparticles can increase the viscosity of the resin, and it will affect the impregnation effect of resin. This phenomenon may cause holes and other defects in the composite materials, and the formation of defects will reduce the interface bonding strength of the composite materials. Tian et al.[17] also had similar conclusions by studying the nanoparticles effect on the properties of the fibers and epoxy resin interface.

4.3 The density of composite and the volume fraction of carbon fiber

As the reinforcement phase, the volume fraction of carbon fiber has a great effect on the mechanical properties of the composites. Kim et al.[18] showed that the tensile strength at the fracture of the composite materials increased from 60MPa to 100MPa when the fiber volume fraction increased from 15% to 45%. This conclusion indicated that the mechanical properties of the composite materials were greatly improved. The density of composites and the volume fraction of carbon fiber at different temperatures are calculated by equations (5) and (6) respectively.[18]

$$\rho_c = \frac{m_c}{v_c} \tag{5}$$

$$v_f = \frac{m_f / \rho_f}{m_c / \rho_c} \times 100\% \tag{6}$$

Where ρ_c (g/cm^3) and m_C (g) are the density and mass of GO-CF/EP composites, v_c (cm^3, obtained by drainage method) is the volume of the composites, v_f is the volume fraction of carbon fiber, m_f (m_f=1.56g) is the mass of carbon fiber, and ρ_f (ρ_f=1.7g/cm^3) is the density of carbon fiber. The calculated data are shown in Table 2.

Table 2. The average mass, volume, density and carbon fiber volume fraction of a single specimen

Extrusion Temperature/℃	Mass /g	Volume/cm^3	Density/g/cm^3	Volume Fraction of Carbon Fiber/%
30	2.34±0.08	1.65±0.05	1.42±0.01	55.50
40	2.15±0.06	1.45±0.05	1.51±0.04	63.00
50	2.24±0.05	1.35±0.05	1.64±0.04	66.30
60	2.28±0.05	1.55±0.05	1.51±0.02	60.00
70	2.98±0.13	2.10±0.05	1.42±0.06	43.00

4.4 Morphology and enhancement of GO

The addition of GO to CFRP can make it disperse evenly in the resin matrix, and some chemical connections among GO, resin and carbon fiber can effectively enhance the interaction.[19] It is found that the dispersion uniformity of GO in the matrix is improved after extrusion, and the distribution trend is closely related to the extrusion direction and the fluidity of the matrix.[13] As shown in Figure 7(a), the micro morphology of GO can be observed by scanning electron microscope. The surface of GO is uneven and has a large number of folds. The fold structure endows GO with a larger surface area, so that it can adhere to the surface of fiber or resin matrix.

The smooth fiber becomes rough and irregular due to the adhesive effect of GO. The adhesion of GO on resin or fiber is shown in Figure 7(b). Fig. 8 shows the schematic diagram of GO playing a role of mechanical locking in GO-CF/EP composites. The contact area between carbon fiber and matrix can be increased and a good interface bonding can be formed by adding GO into the composites. In addition, the special structure of GO makes the mechanical locking between the cured resin and the carbon fiber, thus enhancing the interface bonding strength of the composites. It is helpful to the stress transfer of the materials in the loading process.[19] The maximum stress is often near the interface between the reinforcement and the matrix when the composite is subjected to external force. Ye et al.[20] also obtained a similar conclusion. Therefore, the mechanical lock and structure formed by the addition of GO can increase the maximum stress of the composite to a certain extent. The existence of GO can also reduce the internal stress concentration of the material and play a toughening role, so that the coarse cracks concentrated in the layer can be dispersed into fine slits which can be transferred between layers.[17]

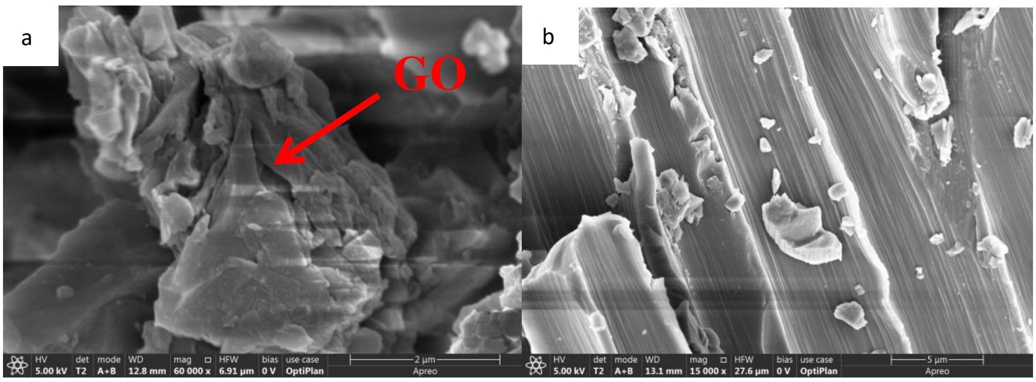

Figure 7. (a)SEM image of GO;　(b) GO attached to the surface of resins or carbon fibers

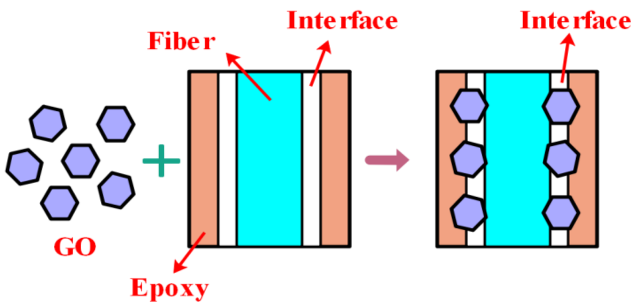

Figure 8. Mechanical locking effect of GO on carbon fibers and resins

4.5 Microstructure and fracture morphology of GO-CF/EP composites

JEOL JSM-6390A scanning electron microscope is used to observe and analyze the fracture mechanism and infiltration of GO-CF/EP composites formed at different extrusion temperatures.

(1) Extrusion temperature 30 °C

Figures 9 (a) and (b) show the microstructure and bending fracture morphology of the composite when the extrusion temperature is 30°C. According to Figure 9 (a), the carbon fiber in the composite structure is black. The surface of the matrix is uneven and slightly bright black. There is matrix distribution in the preform, but the matrix content among the fibers is low. The reason is that the matrix is mostly distributed on the upper and lower surfaces of the composite and among the layers at this temperature, and less matrix infiltrates into the fibers. A large number of fibers are not bonded together, and they are not completely saturated by the matrix. It can be seen from Figure 9 (b) that the fracture surface of the fibers is disordered, and most of the fibers are not bonded by the matrix. The results show that most of the fibers can not bear the load, and can not play a role in strengthening.

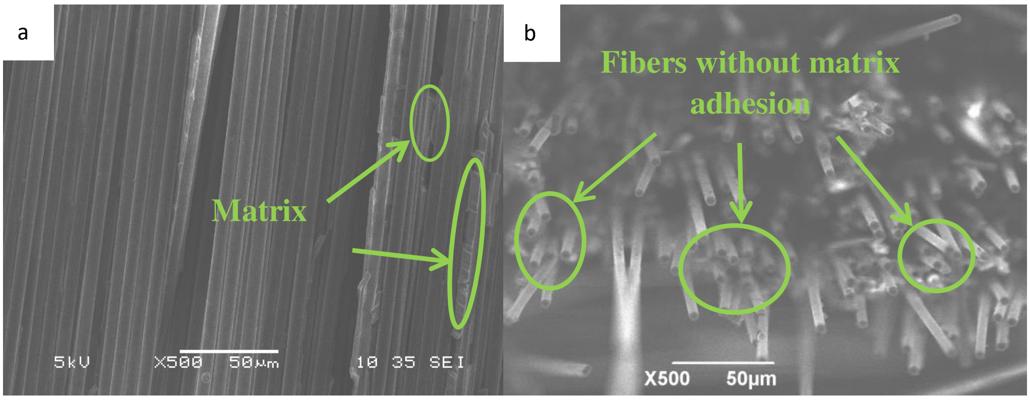

Figure 9. Micrographs of GO-CF/EP composite at 30°C

(a) Infiltration microstructure; (b) Shape diagram of bending fracture

Figure 10 shows the infiltration effect and fracture mode of the composites when the extrusion temperature is 30°C. The viscosity of the matrix is high and the fluidity is poor due to the low extrusion temperature. It is difficult to fully infiltrate the fiber gap in the limited hot-pressing time. Most of the GO is distributed on the surface of the composites or among the fiber layers at this extrusion temperature. There is no GO distributed among the fiber wires and there is less resin. Under this condition, the resin is not bonded to the fiber wires to make them continuous and GO can not make the resin and fibers form a locking structure. Therefore, only a small number of fibers bear the load and a large number of fibers are difficult to transfer the stress under the action of external force. It makes the fibers break at the same time. It can be seen from Table 2 that the density of the composite materials are low at this extrusion temperature, which indicates that there are many pores in the composite materials. When subjected to bending load, the existence of pores also weakens the bearing and transmission of stress in the composite materials. The mechanical properties of the composites are poor at this extrusion temperature according to the above analysis. The bending strength of the composite is only 513MPa according to the three-point bending test results. In order to obtain the composites with compact structure and good mechanical properties, it is necessary to increase the extrusion temperature appropriately, and analyze the relationship between the matrix infiltration distribution in the preform and the bending properties of the materials.

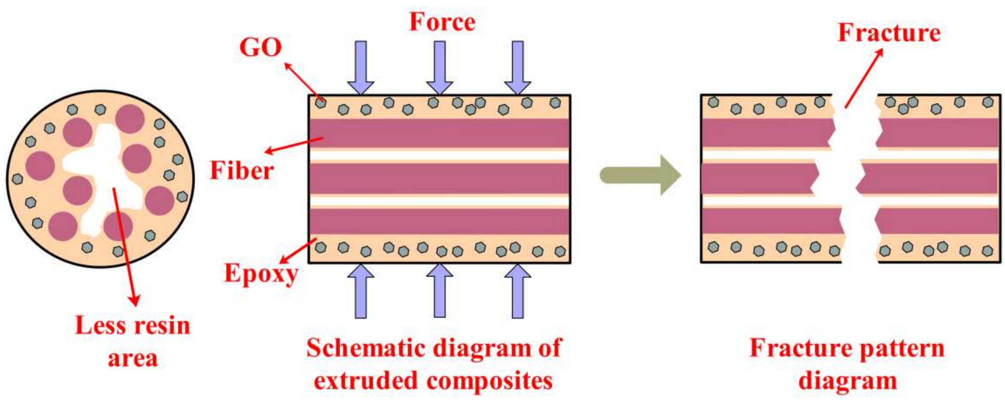

Figure 10. Impregnation effect and fracture mode of GO-CF/EP composites at 30°C

(2) Extrusion temperature 40 °C

Figures 11 (a) and (b) show the infiltration effect and fracture section microstructure of the composite at 40°C. It is found from Figure 11 (a) that the bright black areas in the microstructure increases obviously compared with the microstructure at 30°C. It indicates that the matrix content increases but there is a kind of agglomeration. It can be seen from Figure 11 (b) that the fibers at the fracture section are disorderly fractured and only some fibers are bonded with matrix, which indicates that the matrix infiltration effect is still not ideal although it has been improved.

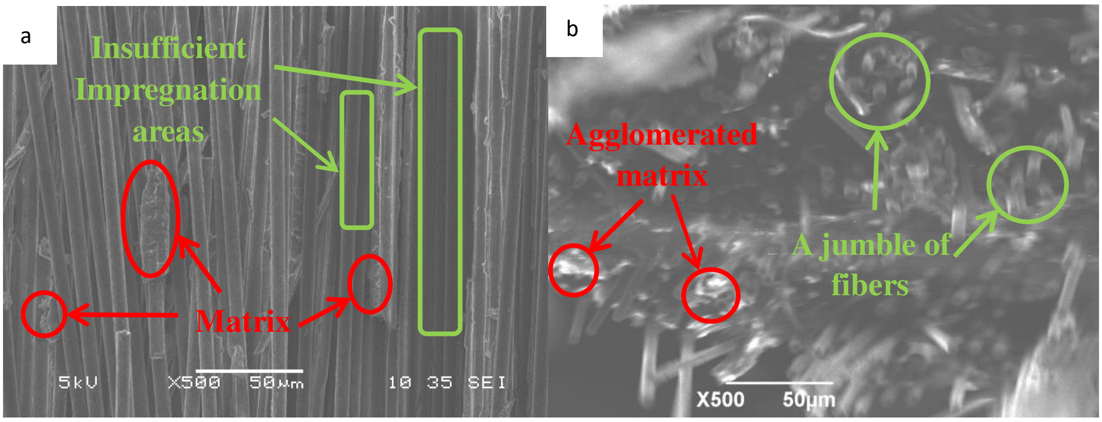

Figure 11. Micrographs of GO-CF/EP composite at 40°C

(a) Infiltration microstructure; (b) Shape diagram of bending fracture

In the process of carbon fiber infiltration, the viscosity of the matrix directly affects the infiltration depth. From equation (7),[21] it can be seen that the infiltration height of the matrix is negatively correlated with the matrix viscosity when the infiltration time is fixed and the fiber volume fraction increases.

$$h = \sqrt{\frac{2K\mathrm{t}\Delta \mathrm{p}}{\mu(1-V_{\mathrm{f}})}} \tag{7}$$

Where h is infiltration height, K is permeability coefficient, t is infiltration time, Δp is viscous pressure drop, μ is matrix viscosity, and V_f is volume fraction of carbon fiber.

The matrix in the composite increases, but the infiltration effect is still not ideal when the extrusion temperature is 40℃. The viscosity of resin decreases with the increase of extrusion temperature. It can be seen from equation (7) that the infiltration height at this time has an increasing trend compared with the extrusion temperature of 30℃, and the matrix fluidity increases. It allows a small amount of GO to flow with the resin and soak into the fiber gaps. Although the independent distribution of most fibers is difficult to effectively bear the load, the overall mechanical properties of the composites are improved to some extent due to the phenomenon of stress transfer on some fibers by the bonding of the matrix and the locking cooperation of GO. The three-point bending test shows that the bending strength is 685MPa, which is significantly higher than 513MPa when the extrusion temperature is 30℃. However, the mechanical properties of the composites are still not ideal. It is necessary to further improve the extrusion temperature to enhance the bearing capacity of the composites.

(3) Extrusion temperature 50℃

Figures 12 (a) and (b) show the microstructure and fracture morphology of the composite when the extrusion temperature increases to 50°C. It can be seen from Figure 12 (a) that the matrix is distributed on a large number of fibers and the matrix agglomeration phenomenon is obviously improved. The infiltration effect is fully uniform at this time. By observing the fracture morphology of the composite shown in Figure 12 (b), it is found that a large number of fibers bonded by the matrix have flat fracture surfaces and it presents obvious characteristics of ductile fracture. There is obvious stress transfer in the process of loading. It will fracture when the load of a part of carbon fibers reach their fatigue load. At this time, the load is transferred to other fibers to enhance the mechanical capacity of the materials and prolong the life of the materials.

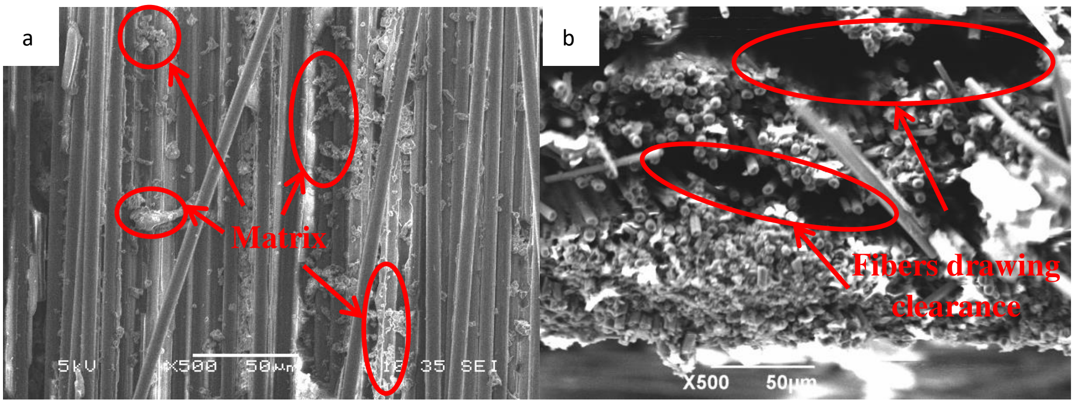

Figure 12. Micrographs of GO-CF/EP composite at 50°C

(a) Infiltration microstructure; (b) Shape diagram of bending fracture

Figure 13 shows the schematic diagram of the infiltration effect, fracture mode and stress transfer of the composites when the extrusion temperature is 50°C. It can be seen from Figure 13 that a large number of uniformly distributed matrix in the fiber layers and fiber gaps of the composites formed at this temperature. The existence of GO makes the resin and carbon fiber fully contact and closely bond, and enhances the interface bonding energy between the matrix and the reinforcement. When an external force is applied to the composite materials, the stress is transferred from one part of the fibers to other fibers through the resin. GO also bears part of the load in the process of stress transfer. At this time, the internal structure of the composites are in an ideal state. It can be seen from the data in Table 2 that the density and carbon fiber volume fraction of the composites reach the maximum at this extrusion temperature. Analyzing the reasons, the increase of temperature makes the matrix flow ability stronger. The matrix filled inside the composite materials under a certain pressure and the density of the composite is increased. The bending strength is 977MPa, which shows that the mechanical properties of the composites are greatly improved. In order to determine the optimal extrusion parameters, it is necessary to continue to increase the temperature and further analyze the internal structure and mechanical properties of the materials.

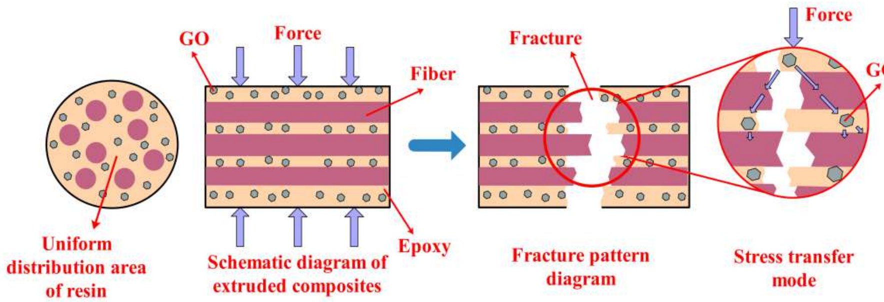

Figure 13. Impregnation effect, fracture mode and the model of stress transfer of GO-CF/EP composites at 50°C

(4) Extrusion temperature 60°C

When the extrusion temperature is 60°C, the microstructure and fracture morphology of the composite are observed as shown in Figures 14 (a) and (b). It can be seen from Figure 14 (a) that most of the matrix is agglomerated in the internal structure of the composite. The reason for this phenomenon is that the fluidity of the matrix is greatly improved with the increase of temperature and the curing speed is also accelerated. This phenomenon makes the matrix not fully filled with the internal gaps of the fibers, but the phenomenon of curing occurs. By observing Figure 14 (b), it is found that the matrix is unevenly distributed on the fibers. The fracture surface of the fiber is even. There are some zigzag cracks in the fracture section, which are mainly distributed near the matrix aggregation area.

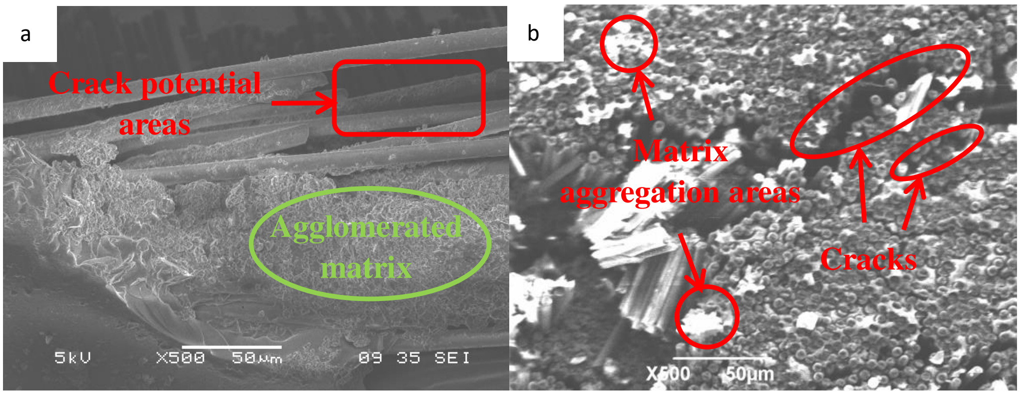

Figure 14. Micrographs of GO-CF/EP composite at 60℃

(a) Infiltration microstructure; (b) Shape diagram of bending fracture

When the temperature rises to 60℃, the uneven distribution and agglomeration of the matrix lead to micro pores in the composites. The fibers near the matrix aggregation areas can not effectively play the role of bearing the load due to the absence of resin adhesion under the load, and GO can not disperse the stress, which leads to the stress concentration failure of these pores and gradually expand into cracks. It can be seen from the data in Table 2 that the density and fiber volume fraction of the composites decrease when the extrusion temperature is 60℃. The bending strength of the composite under this condition is 718 MPa, which is significantly lower than that of the composite when the extrusion temperature is 50℃. The results show that the curing speed of the matrix is accelerated and it results in the aggregation of some resins with the increase of extrusion temperature. This phenomenon reduces the load transfer capacity of the composites and causes cracks and other defects. In order to further determine the effect of extrusion temperature on the composites, the temperature value should be continuously increased to observe the change of infiltration effect and bending properties of the composites.

(5) Extrusion temperature 70°C

As shown in Figures 15 (a) and (b), the infiltration situation and bending fracture mechanism at extrusion temperature of 70°C are analyzed. According to the microstructure shown in Figure 15 (a), it is found that the matrix agglomeration is in the internal structure. In addition, the content of matrix is significantly reduced and no resin adheres to the fibers. According to the observation in Figure 15 (b), the matrix distribution at the fracture is extremely uneven and the number of cracks is significantly increased. The fracture is even and shows the characteristics of brittle fracture when the fibers break. It indicates that fibers can not play a good bearing capacity under this condition.

The thickness of the composites increases when the extrusion temperature is 70°C. The reason for this phenomenon is that GO is dispersed in alcohol to form GO suspension in the process of preparing solution. However, the alcohol in the suspension is not completely removed by ultrasonic dispersion and vacuum treatment, so that there are still bubbles generated by alcohol in the composites. These bubbles will burst when the temperature rises to a certain value, which will lead to the increase of the size of the material in the thickness direction. Figure 16 shows the infiltration effect, fracture mode and stress transfer mode of the composites when the extrusion temperature is 70°C. When the composite is at this extrusion temperature, the matrix is partially squeezed out due to the significant improvement of fluidity, which directly leads to the appearance of less matrix areas in the composite. According to the research of Ye et al.,[22] it is found that these areas with less resin are mainly elliptical pores that parallel to the fiber direction. The appearance of these areas is a direct factor for the existence of cracks. However, it is not difficult to find that cracks are narrow and tortuous at this extrusion temperature, because the crack direction is deflected by the existence of GO and effectively reduces the stress concentration. According to Table 2, the density of the composites and volume fraction of carbon fiber decrease obviously at this extrusion temperature. The bending strength of the composite material is 760MPa. The mechanical properties are improved because of the influence of thickness. With the increase of extrusion temperature, the fluidity of the matrix is good, but the phenomenon of agglomeration appears. It will cause defects in the internal structure of the composite materials.

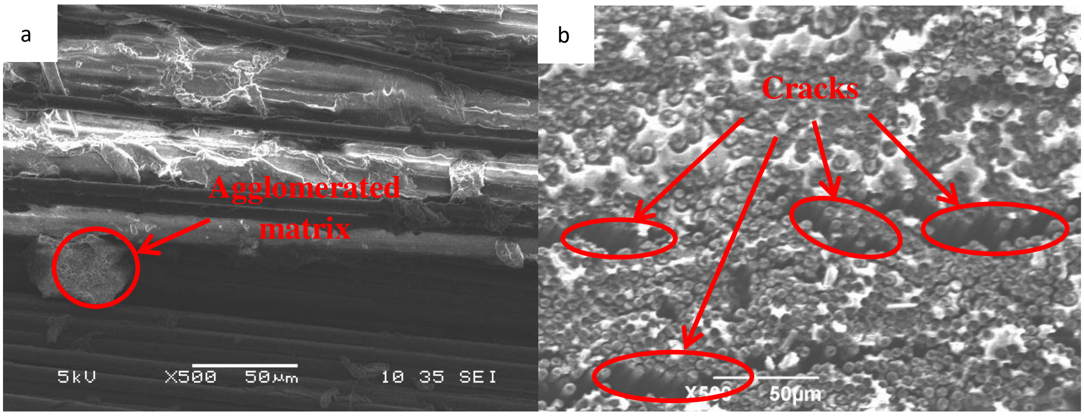

Figure 15. Micrographs of GO-CF/EP composite at 70°C

(a) Infiltration microstructure; (b) Shape diagram of bending fracture

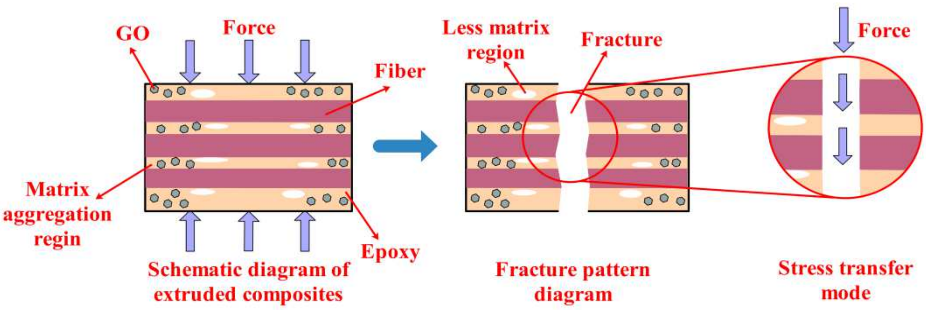

Figure 16. Impregnation effect, fracture mode and the model of stress transfer of GO-CF/EP composites at 70°C

By analysing of the microstructure mechanism and fracture morphology of the composites formed at different extrusion temperatures, it is found that the infiltration effect of the matrix presents a uniform trend with the increase of extrusion temperature. When the extrusion temperature reaches 50℃, the infiltration effect of the matrix in the fiber is the best and the mechanical properties of the composites at this time are significantly higher than those at other temperatures. However, the fluidity of the matrix can not form a good matching relationship with the curing time and only a few fibers are glued by the matrix when the extrusion temperature is high. This phenomenon reduces the mechanical properties. In addition, a high extrusion temperature will cause cracks and other defects in the composites. These defects will seriously affect the loading capacity of composites.

5. Conclusion

(1) Graphene oxide-carbon fiber hybrid reinforced composites with resin as matrix, GO and carbon fiber as reinforcement materials can be prepared by vacuum infiltration hot-pressing molding process. The surface morphology of the composites is good, and no obvious defects are found such as holes and warpage.

(2) The addition of GO increases the contact areas between the resin and carbon fiber, which makes them form physical mechanical locks. The appearance of this structure significantly enhances the interfacial bonding ability of the composites. When the composite is subjected to external force, GO bears part of the stress. This phenomenon reduces the stress concentration in the crack areas and makes the cracks deflected, which significantly improves the mechanical properties of the composites.

(3)The matrix was evenly distributed among the carbon fibers when the extrusion temperature was 50℃. GO not only bonded the resin and carbon fibers together by mechanical locking, but also effectively shared the load. Due to the bonding effect of resin, the fibers could give full play to their load-bearing capacity, and most of the fibers were pulled out or broken when they broke. The bending strength at this extrusion temperature was 977MPa by the three-point bending test.

(4) It is found that too high or too low extrusion temperature will affect the internal microstructure and mechanical properties of composites. The viscosity of the matrix is high and the flow rate is slow when the extrusion temperature is low, which leads to the agglomeration, solidification and dispersion of the matrix. Most of the matrix and fibers can not give full play to their respective roles. In this case, the bending strength of the composite is low. When the extrusion temperature is high, the matrix is partially extruded due to its excellent fluidity and the ability of resin to transfer load is weakened. The ability of GO to share stress is also weakened, and it results in poor mechanical properties of the materials. Therefore, it is the key to control the extrusion temperature in the process of materials forming to prepare excellent composites.

Availability of data and materials

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

Competing interests

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Y.M. reports financial support was provided by National Natural Science Foundation of China. Y.M. reports financial support was provided by Ministry of education production university cooperation education project of China. Y.M. reports financial support was provided by New experiment and equipment development project of Xidian University.

Funding

This paper is supported by the following funds, the National Natural Science Foundation of China (grant number 51705389), the Ministry of education production university cooperation education project of China (grant number 201902004016), Natural Science Foundation of Shanxi Province (grant number 2020JM-200), the New experiment and equipment development project of Xidian University (grant number SY1954) and the Fundamental Research Funds for the Central Universities and Innovation Fund of Xidian University (grant number 5004-20109195867 and 5004-20109205867).

Authors' contributions

Conceptualization, Y.M. and L.Y.; Investigation, Y.M. and W.X.; Data curation, H.G., Y.L., M.C. and H.J.; Writing-original draft, F.L.; Writing-review & editing, Y.M. and F.L.; Supervision, Y.M., W.X. and L.Y.

Acknowledgments

The authors are grateful for the financial support from the National Natural Science Foundation of China (grant number 51705389). This study was funded by the Ministry of education production university cooperation education project of China (grant number 201902004016), Natural Science Foundation of Shanxi Province (grant number 2020JM-200), the New experiment and equipment development project of Xidian University (grant number SY1954), and the Fundamental Research Funds for the Central Universities and Innovation Fund of Xidian University (grant number 5004-20109195867 and 5004-20109205867).

Reference

[1] Pumera M. Electrochemistry of graphene, graphene oxide and other graphenoids: Review[J]. ELECTROCHEM COMMUN, 2013, 36: 14-18.

[2] Heo Y, Im H, Kim J, et al. The influence of Al(OH)3-coated graphene oxide on improved thermal conductivity and maintained electrical resistivity of Al2O3/epoxy composites[J]. J NANOPART RES, 2012, 14(10): 1196.

[3] Suner S, Joffe R, Tipper JL, et al. Ultra high molecular weight polyethylene/graphene oxide nanocomposites: Thermal, mechanical and wettability characterisation[J]. COMPOS PART B-ENG, 2015, 78: 185-191.

[4] Lee YH, Polavarapu L, Gao NY, et al. Enhanced optical properties of graphene oxide-Au nanocrystal composites[J]. LANGMUIR, 2012, 28(1): 321-326.

[5] Chen J, Zhao D, Ge HY, et al. Graphene oxide-deposited carbon fiber/cement composites for electromagnetic interference shielding application[J]. CONSTR BUILD MATER, 2015, 84: 66-72.

[6] Stankovich S, Richard DP, Nguyen ST, et al. Synthesis and exfoliation of isocyanate-treated graphene oxide nanoplatelets[J]. CARBON, 2006, 44(15): 3342-3347.

[7] Chen JL, Dai FF, Zhang LL, et al. Molecular insights into the dispersion stability of graphene oxide in mixed solvents: Theoretical simulations and experimental verification[J]. J COLLOID INTERF SCI, 2020, 571: 109-117.

[8] Paredes JI, Villar-Rodil S, Martinez-Alonso A, et al. Graphene oxide dispersions in organic solvents[J]. LANGMUIR, 2008, 24(19): 10560-10564.

[9] Ma YQ, Zhao YT, Zhang Y, et al. Influence of infiltration pressure on the microstructure and properties of 2D-CFRP prepared by the vacuum infiltration hot pressing molding process[J]. POLYMERS-BASEL, 2019, 11(12): 2014.

[10] Yousefi AM, Love BJ. Probing the temperature sensitivity of induction time in latent cure epoxy resins[J]. POLYM INT, 2013, 62(10): 1451-1456.

[11] Fard RR, Akhlaghi F. Effect of extrusion temperature on the microstructure and porosity of A356-SiCp composites[J]. J MAYER PROCESS TECH, 2007, 187: 433-436.

[12] Wang XJ, Nie KB, Hu XS, et al. Effect of extrusion temperatures on microstructure and mechanical properties of SiCp/Mg–Zn–Ca composite[J]. J ALLOY COMPD, 2012, 532: 78-85.

[13] Shao PZ, Chen GQ, Ju BY, et al. Effect of hot extrusion temperature on graphene nanoplatelets reinforced Al6061 composite fabricated by pressure infiltration method[J]. CARBON, 2020, 162: 455-464.

[14] Ma YQ, Qi LH. Effect of extrusion temperature on the microstructure and tensile property of 2D-Cf/Al composites by liquid extrusion infiltration[J]. INT J ADV MANUF TECH, 2018, 94(1-4): 1349-1355.

[15] Ma YQ, Wang J, Zhao YT, et al. A new vacuum pressure infiltration CFRP method and preparation experimental study of composite[J]. POLYMERS-BASEL, 2020, 12(2): 419.

[16] Guo ZS, Du SY, Zhang BM, et al. Curekinetics and chemo rheological behavior of epoxy resin used in advanced composites. Acta Mater Compos Sin, 2004, 21(4); 146-151.

[17] Tian Y, Zhang H, Zhang Z. Influence of nanoparticles on the interfacial properties of fiber-reinforced-epoxy composites[J]. COMPOS PART A-APPL S, 2017, 98: 1-8.

[18] Kim YH, Choi C, Kumar SSK, et al. Thermo-gravimetric analysis method to determine the fiber volume fraction for PAN-based CFRP considering oxidation of carbon fiber and matrix[J]. COMPOS PART A-APPL S, 2017, 102: 40-47.

[19] Pathak AK, Borah M, Gupta A, et al. Improved mechanical properties of carbon fiber/graphene oxide-epoxy hybrid composites[J]. COMPOS SCI TECHNOL, 2016, 135: 28-38.

[20] Ye JJ, Wang YW, Li ZW, et al. Failure analysis of fiber-reinforced composites subjected to coupled thermo-mechanical loading. COMPOS STRUCT, 2020, 235: 111756.

[21] Lin XT, Chu SJ, Wang HW. Design of counter pressure infiltration and solidification equipment of metal matrix composite. China Mech Eng, 1996, 7: 53-55.

[22] Ye JJ, Cai H, Liu L, et al. Microscale intrinsic properties of hybrid unidirectional/woven composite laminates: Part I experimental tests. COMPOS. STRUCT, 2020, 113369.

Figures

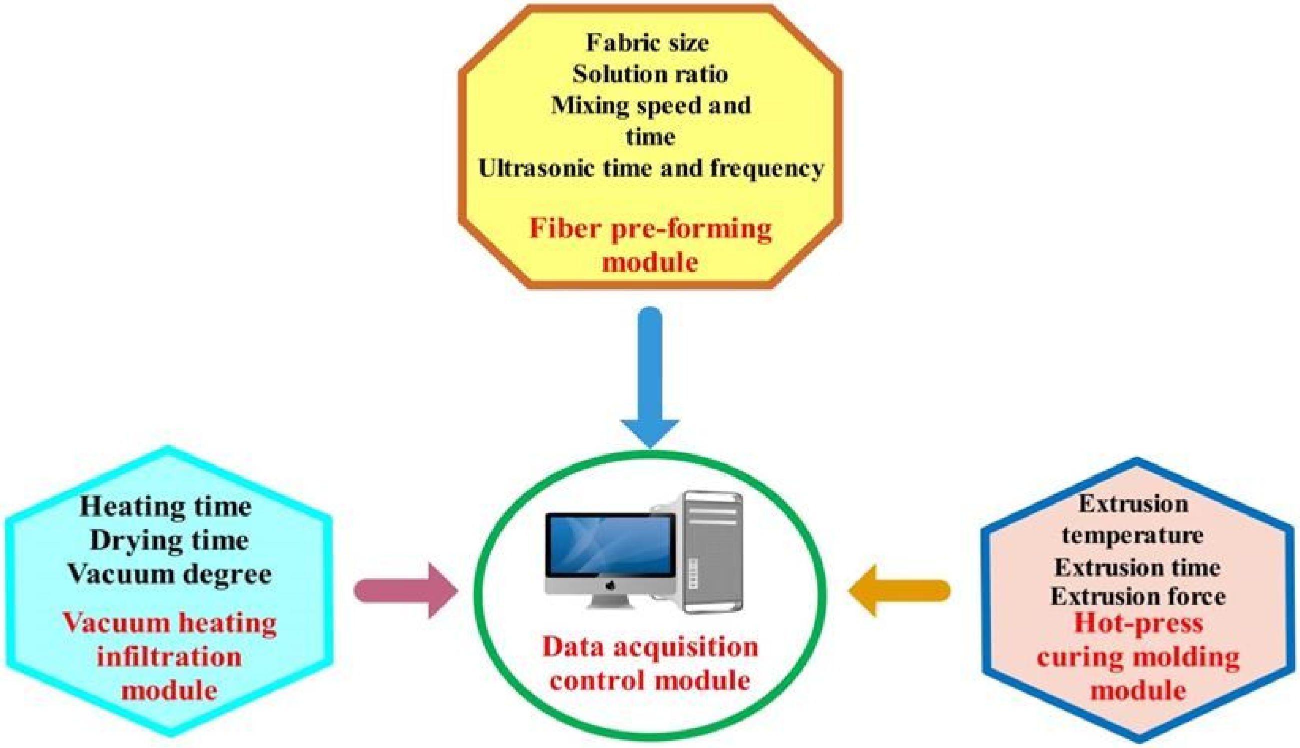

Figure 1

Vacuum infiltration hot-pressing experimental system

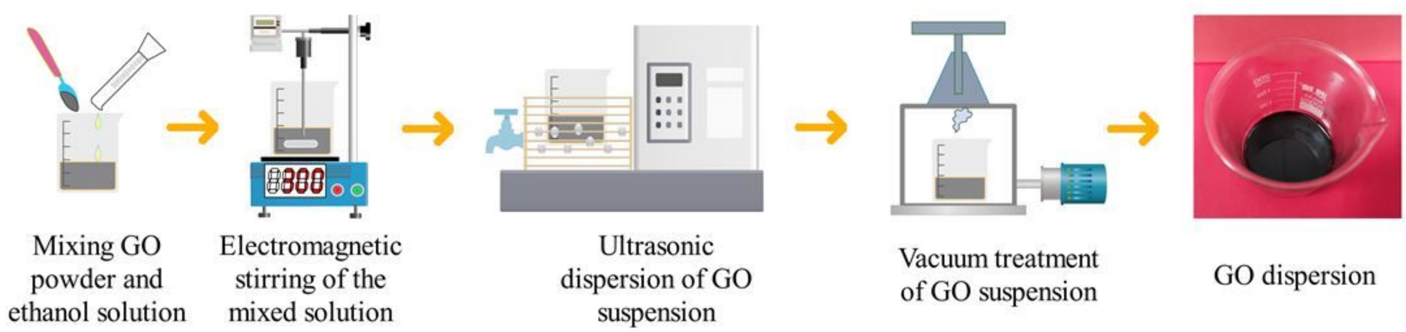

Figure 2

Preparation process of GO dispersion

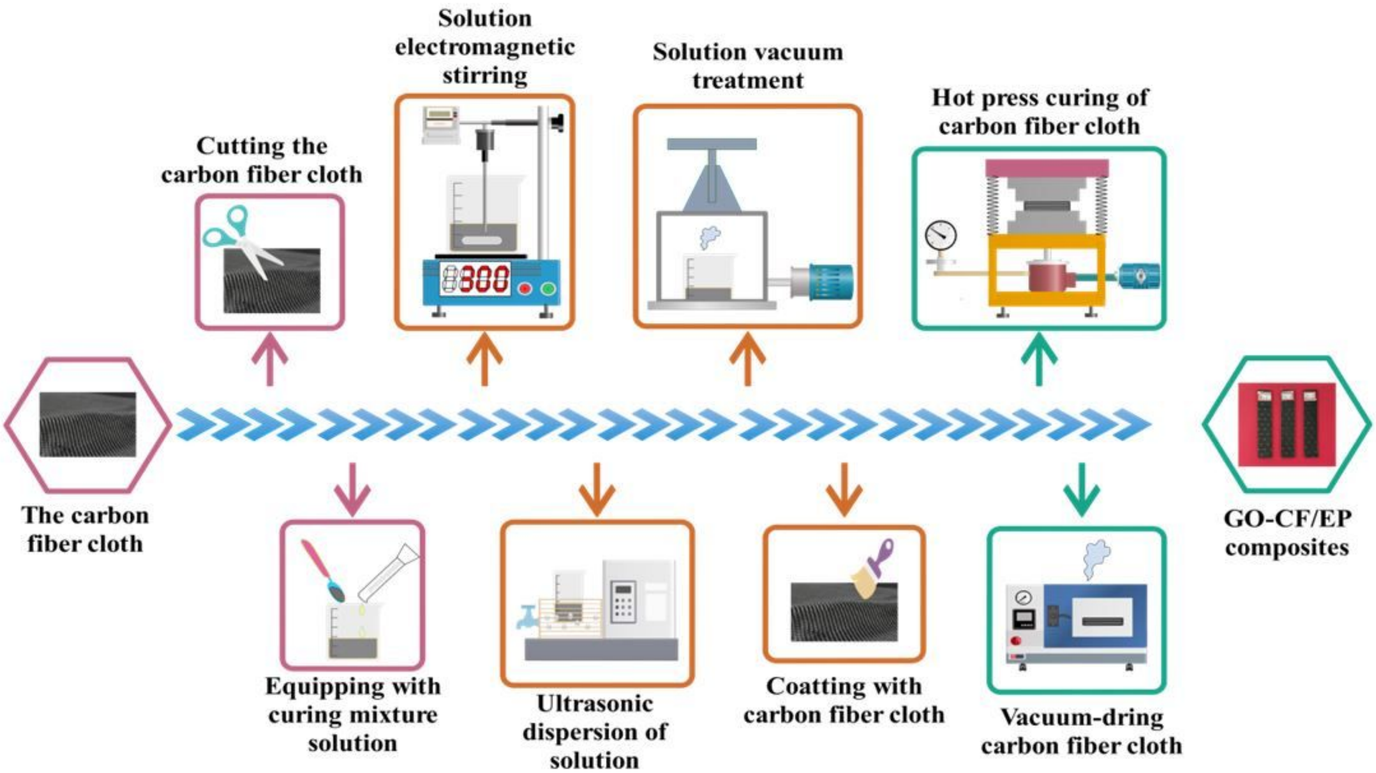

Figure 3

Preparation process of GO-CF/EP composites

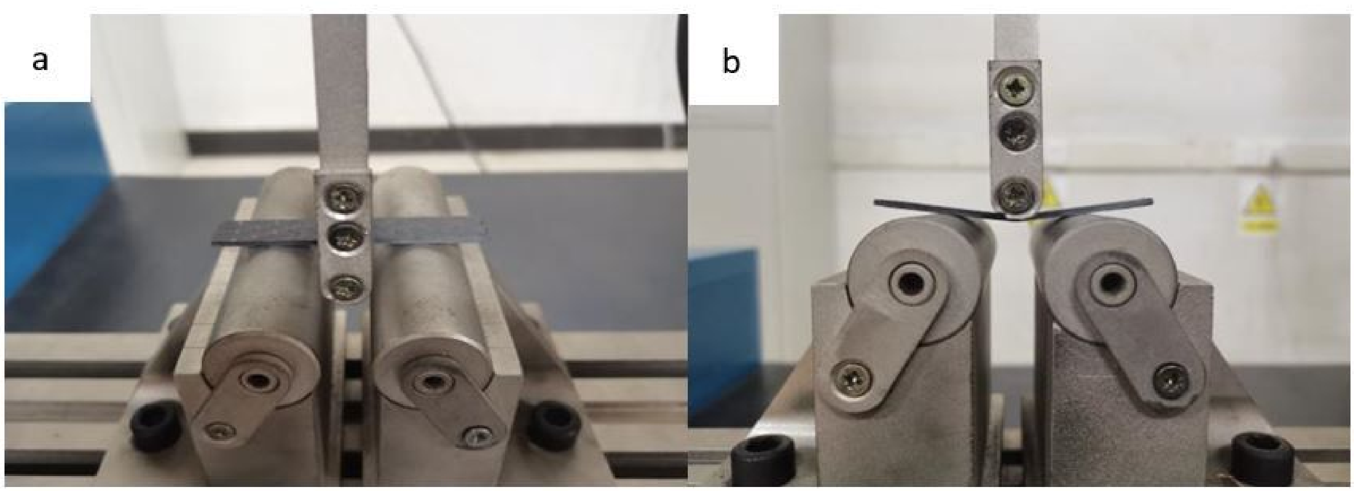

Figure 4

Loading diagram of three-point bending

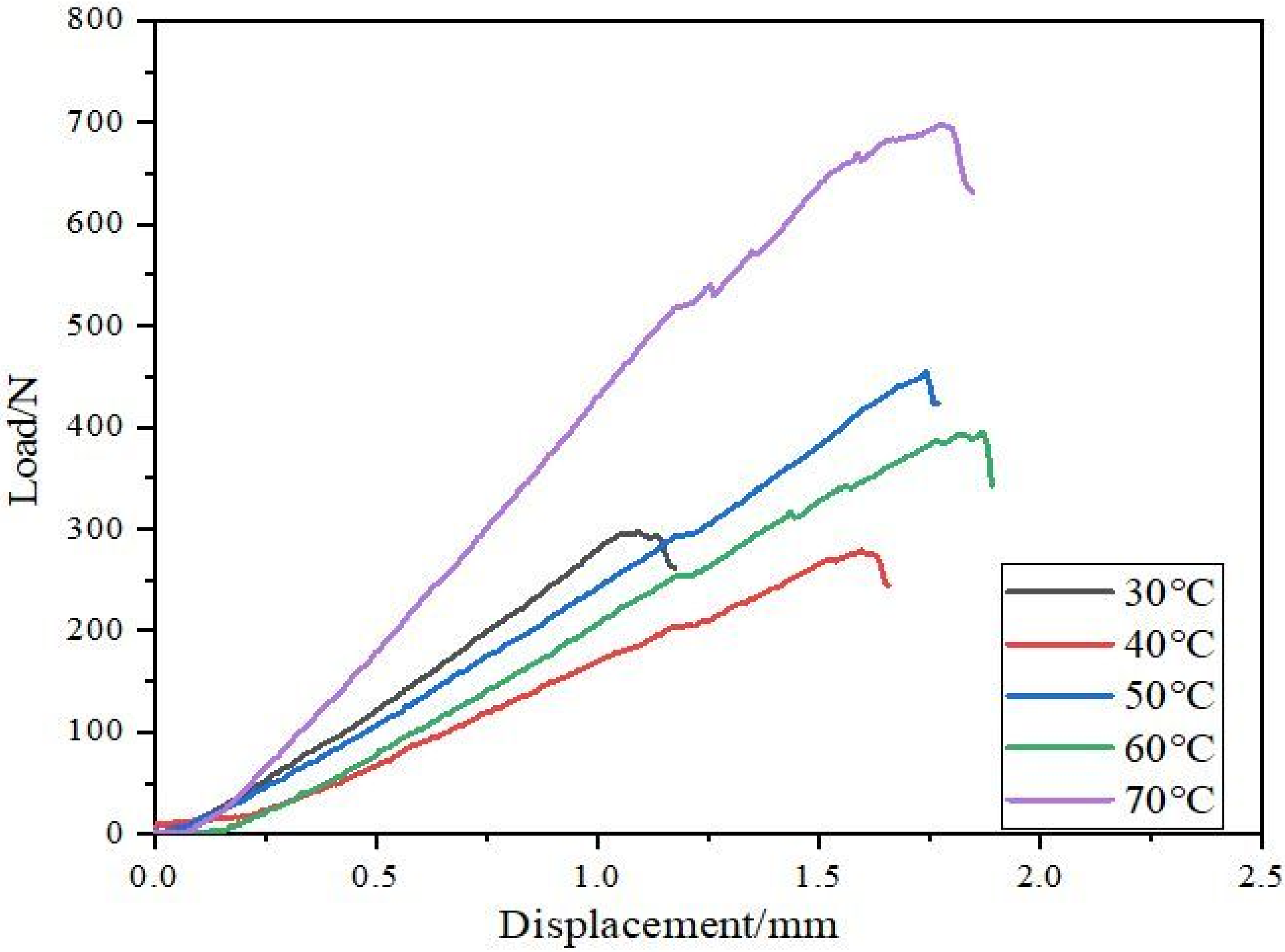

Figure 5

Load - displacement curves of composites at different extrusion temperatures

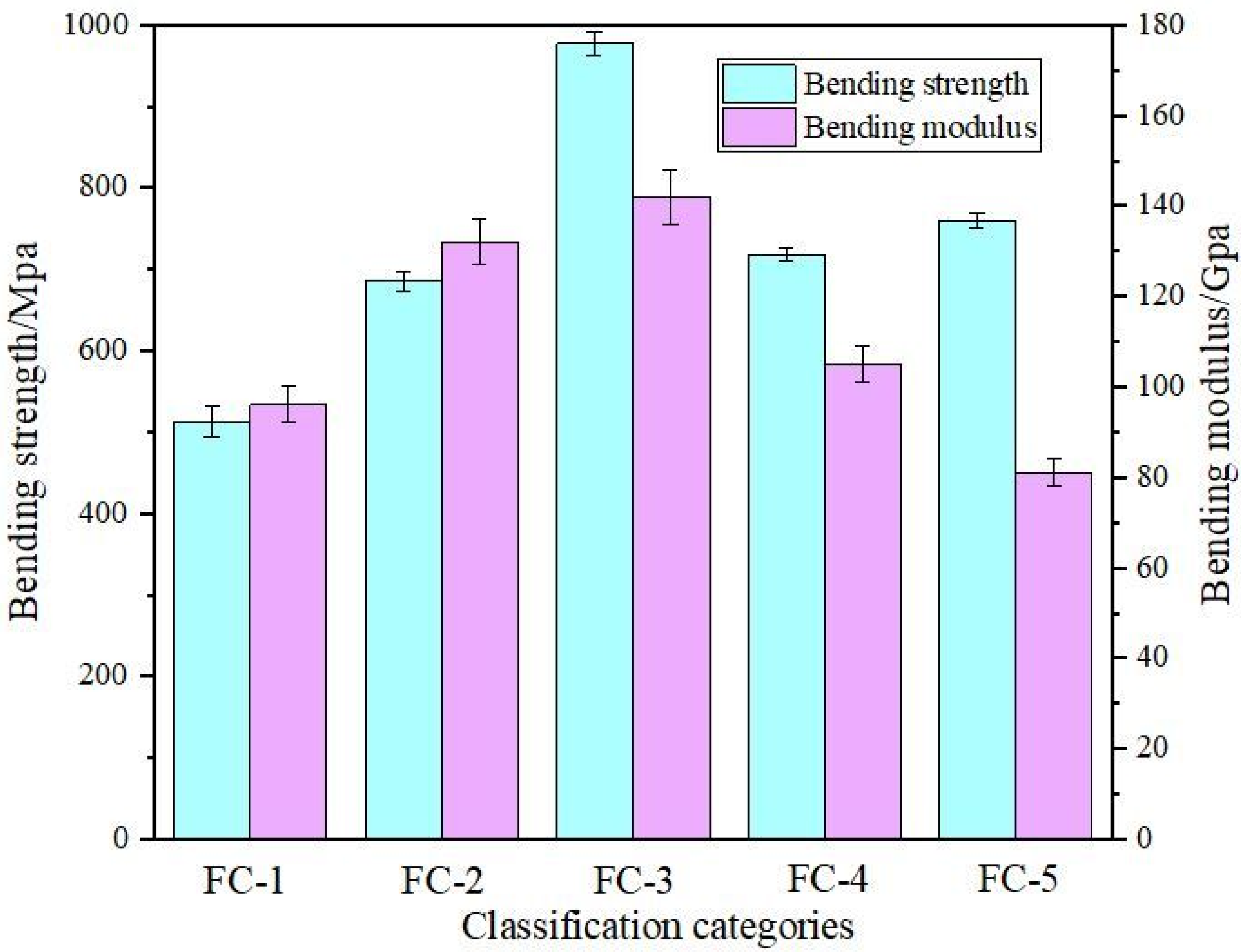

Figure 6

The bending strength and bending modulus of the composites at different extrusion temperatures

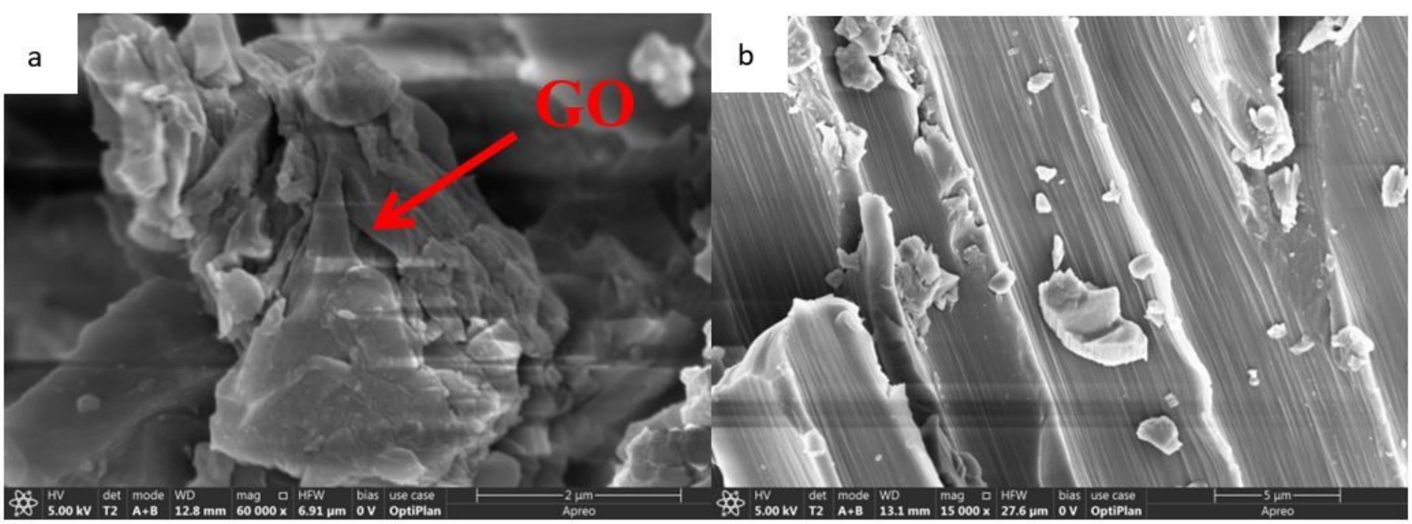

Figure 7

(a)SEM image of GO; (b) GO attached to the surface of resins or carbon fibers

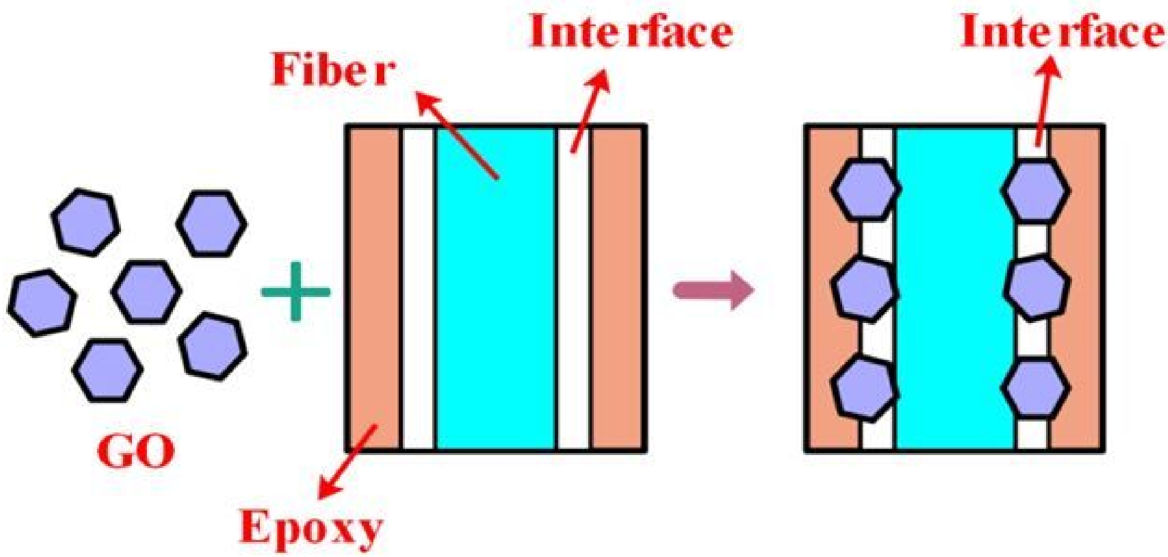

Figure 8

Mechanical locking effect of GO on carbon fibers and resins

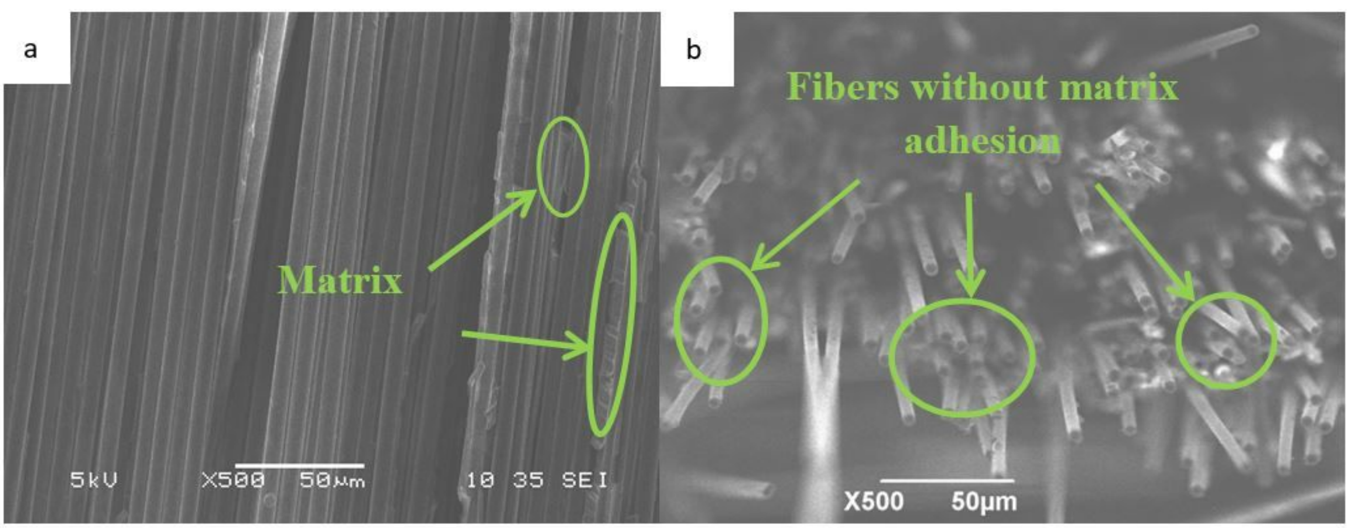

Figure 9

Micrographs of GO-CF/EP composite at 30 (a) Infiltration microstructure; (b) Shape diagram of bending fracture

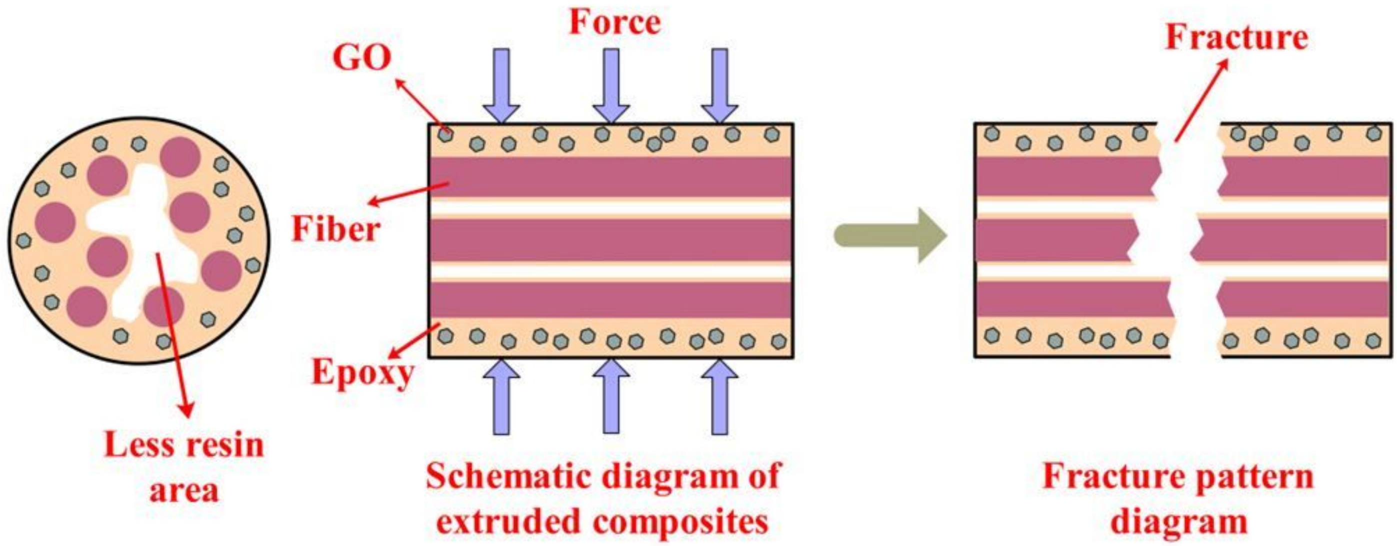

Figure 10

Impregnation effect and fracture mode of GO-CF/EP composites at 30

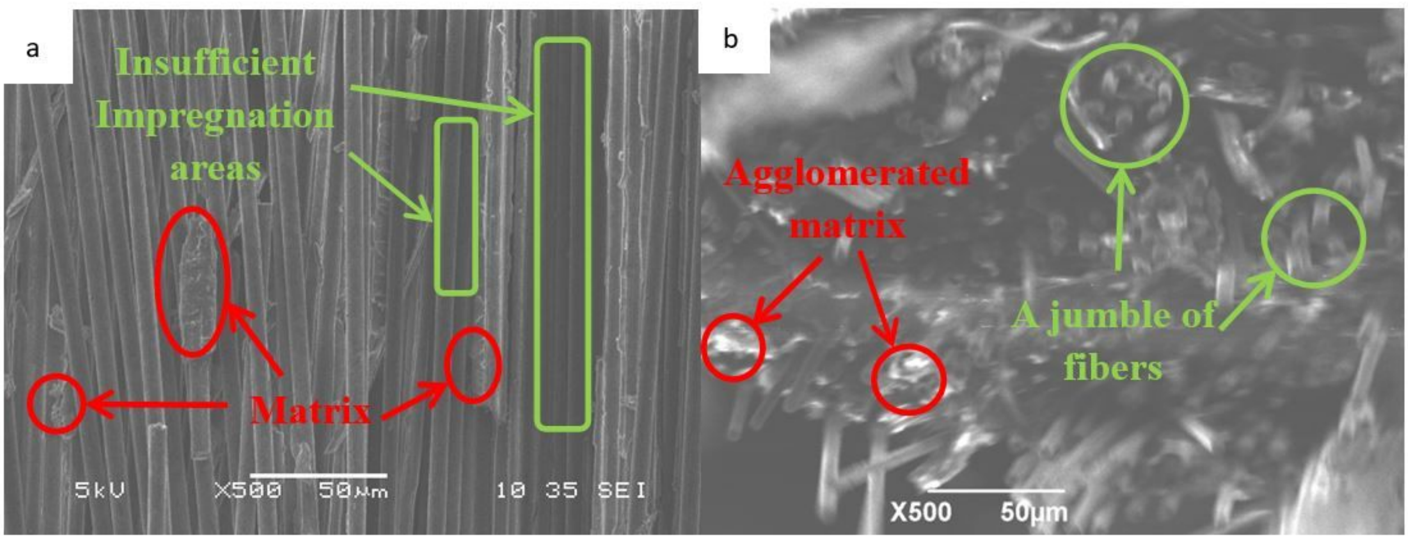

Figure 11

Micrographs of GO-CF/EP composite at 40 (a) Infiltration microstructure; (b) Shape diagram of bending fracture

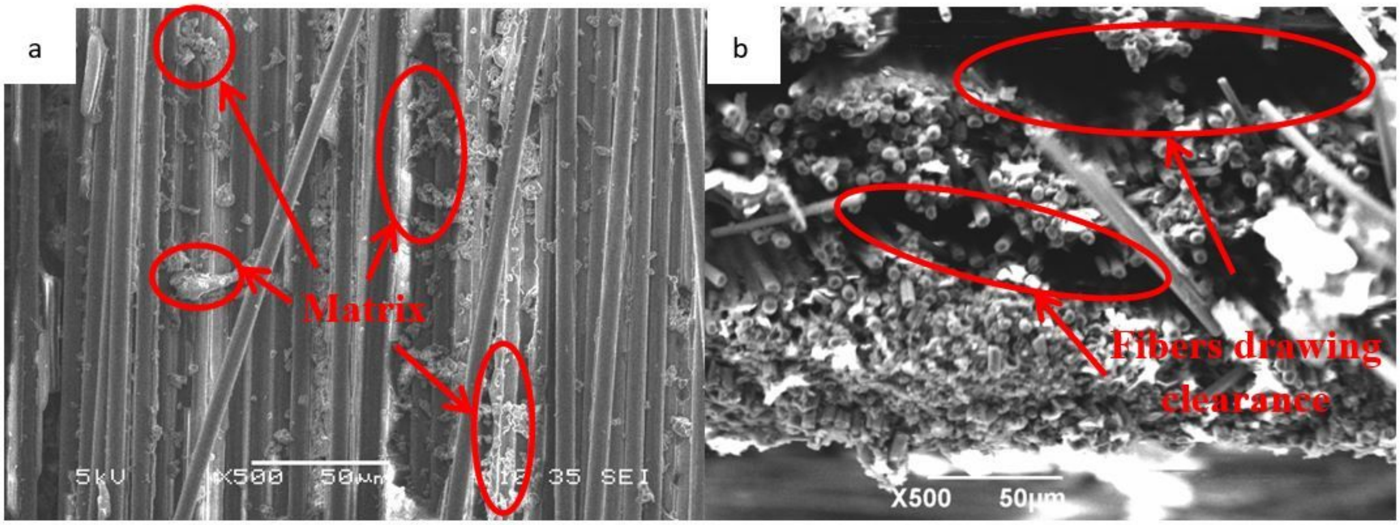

Figure 12

Micrographs of GO-CF/EP composite at 50 (a) Infiltration microstructure; (b) Shape diagram of bending fracture

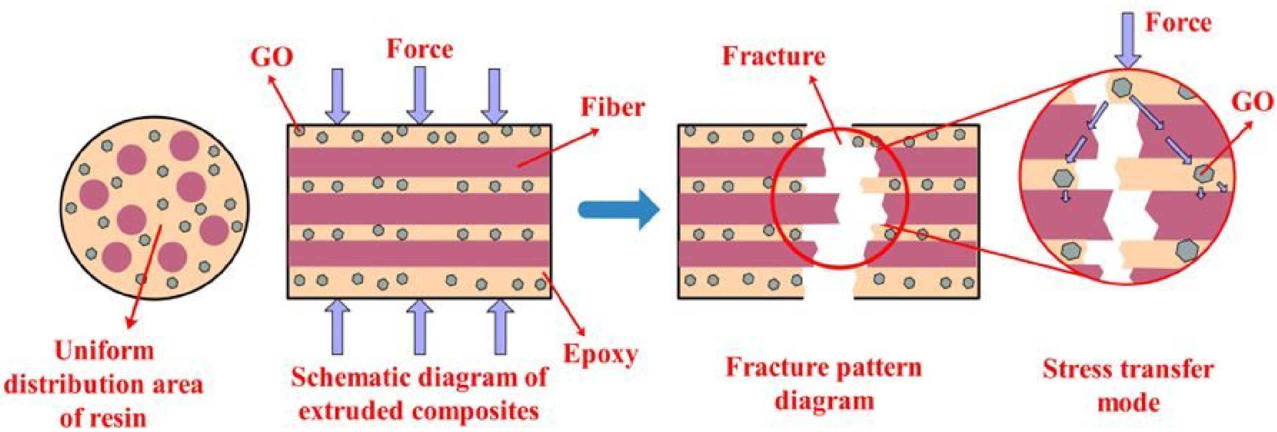

Figure 13

Impregnation effect, fracture mode and the model of stress transfer of GO-CF/EP composites at 50

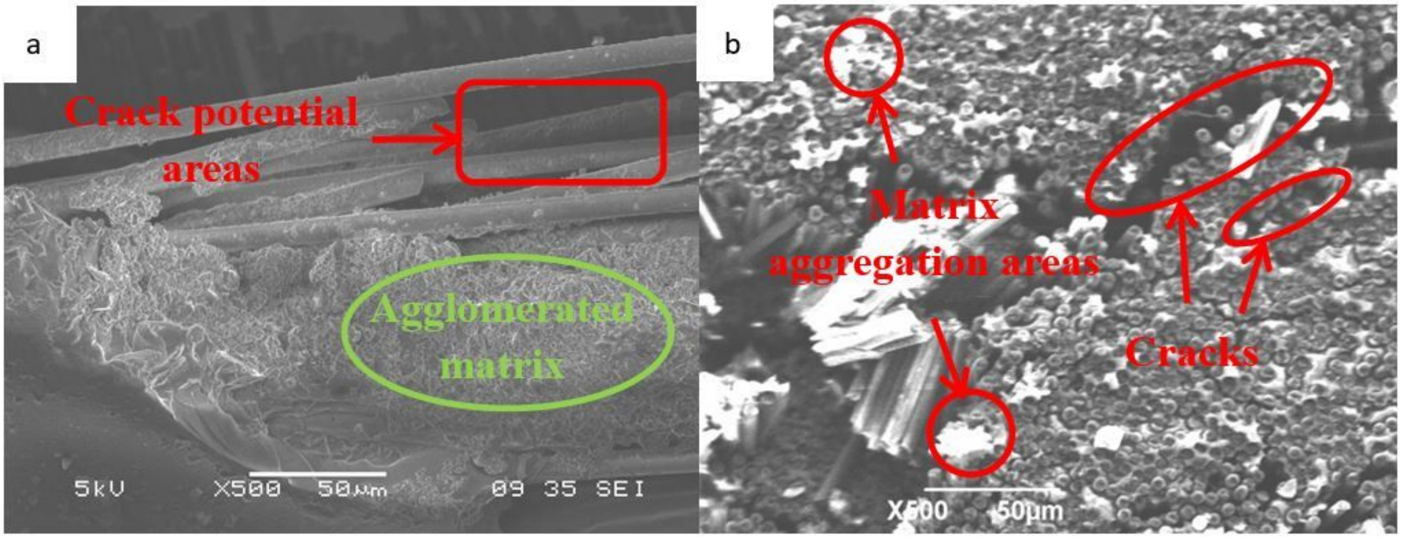

Figure 14

Micrographs of GO-CF/EP composite at 60℃ (a) Infiltration microstructure; (b) Shape diagram of bending fracture

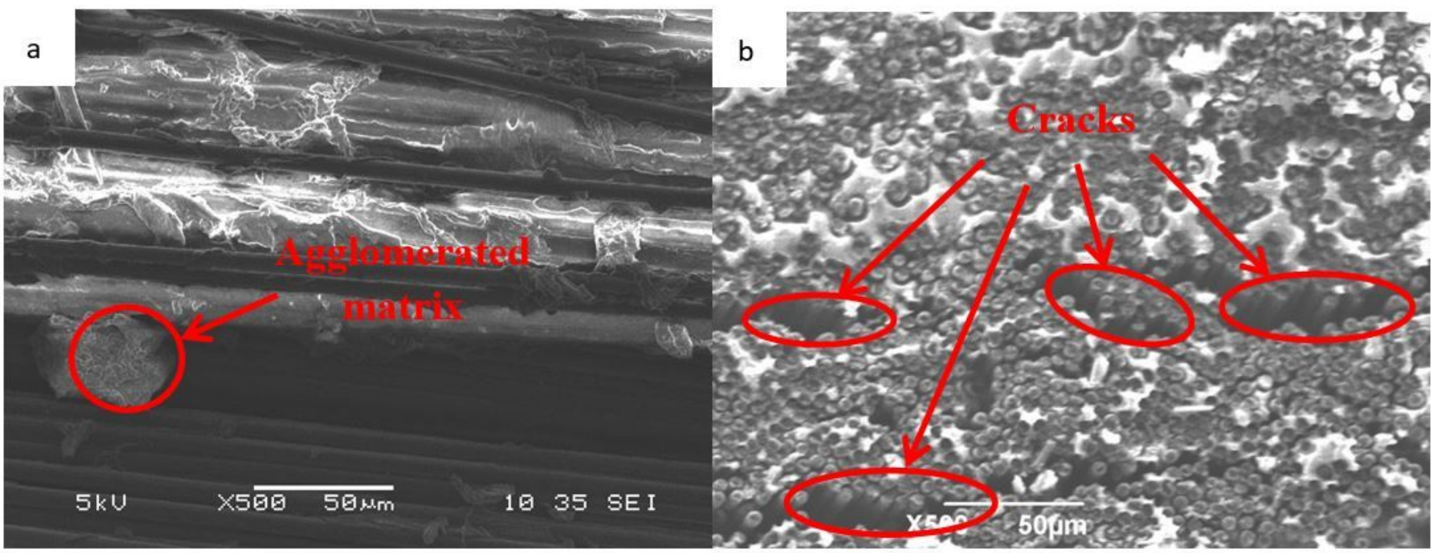

Figure 15

Micrographs of GO-CF/EP composite at 70℃ (a) Infiltration microstructure; (b) Shape diagram of bending fracture

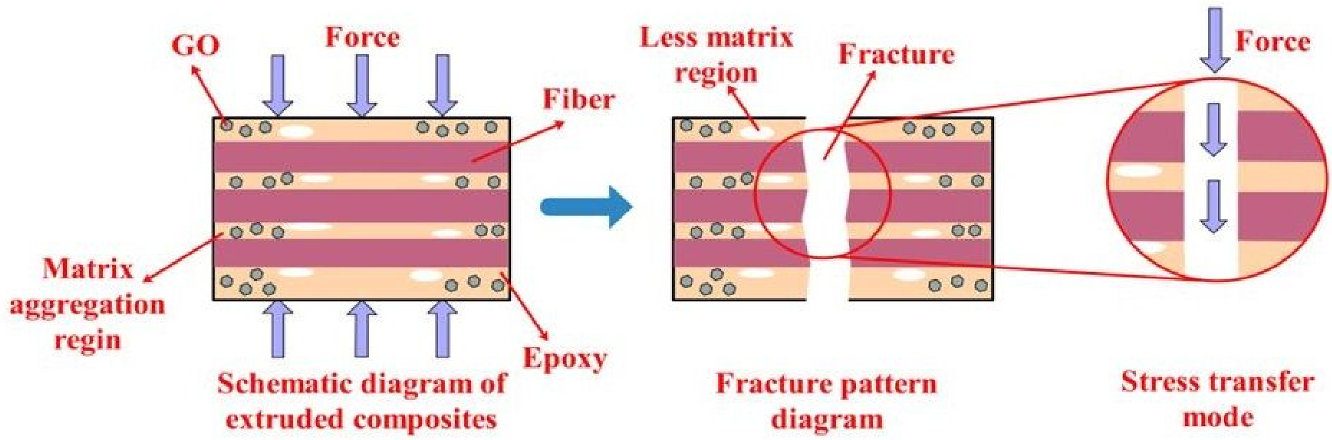

Figure 16

Impregnation effect, fracture mode and the model of stress transfer of GO-CF/EP composites at 70℃