Review

Interfacial characterization, control and modification of carbon fiber reinforced polymer composites

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ABSTRACT

Fibrous carbon materials have been attracted many researchers' attentions. Carbon fibers have been developed as one of the most important industrial materials for modern science and technology since 1960s [1]. Due to the superior mechanical properties including high-specific strength and modulus, low density and thermal expansion, heat resistance, and chemical stability, carbon fibers as reinforcement materials have provided the impetus for researchers in developing high-performance composite materials. Nowadays, carbon fiber reinforced plastics (CFRP) are widely applied in the industries of aeronautic, aerospace, sporting goods, as well as new energy.

The region between the fibers and matrix, contains unique micromechanical properties, is characteristically called the interphase and influence the bulk composite properties. Interface between fibers (reinforcements) and matrix is an important component for CFRP which may govern the CFRP performances [2]. For example, the interphase determines the off-axis strength and impact toughness of CFRP, environmental stability of CFRP and functional performance of CFRP. The effect of interface on composite can be achieved by regulating the composition, structure and distribution of the interface [3]. It has been proved that there has an optical interface for polymer based composite through the match of composite interface, reinforcement and polymer matrix. However, in terms of the smooth surface and chemical inertness of carbon fiber, the interface between carbon fiber and resin matrix is unsatisfactory. The interface should be modified and carefully controlled, which can be through by increasing the surface polarity of carbon fiber, improving the wettability between carbon fiber and resin, as well as promoting the chemical reaction. Obey these principles, the interfacial modification methods have been well developed.

The universality of carbon fiber and polymer matrix, and the variability of the composite material forming process result in the complexity of polymer-based composites interface problems. Meanwhile the scale of the interface region is very small, it has great difficulty in characterizing the chemical structure, physical properties and mechanical characteristics. Recently, a series of effective characterization methods have been developed and initial interface characterization system is always being improved. With interface characterization techniques, the interfacial composition, structure morphology and micro-mechanical characteristics of interface can be researched easily, which can provide the basis for studying the interface physical and chemical properties. Hence interface characterization techniques not only are theory researches, but also have important practical significance for solving practical application problems of carbon fiber composites. Interface characterization techniques have become an important research direction of interface engineering research.

In this paper, the researches in this field of carbon fiber interface were described, such as carbon fiber composite material characterization methods, interface control, and interfacial modification methods. With reference to the research achievements of a large number of scholars at present, so their current development trend were systemic concluded.

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Contents

1. Interfacial characterization of FRP

Interfacial characterizations are used to acknowledge the function of interface and the influence of the interfacial structure on material overall performances. It mainly includes characterization of interfacial chemical and physical structure, thickness and morphology, adhesion strength and residual stress. Based on these characterized results, the relationship between interface performance and the composite material performance can be clarified. Nowadays, the scientific development provides a powerful mean to characterize the interface of composite materials, and some of the advanced technologies have been applied in the composite interface analysis, which contributes to revealing the nature of the interface and enriching the theoretical research of the interface. However, due to the micro area and the complicated structure of the interface, the studies on characterization methods of composite material interface, which are comprehensive and accurate, have been the difficulties and hot spots in the field of composite material interface research.

1.1. Characterization on interfacial adhesion of FRP

Characterization of interfacial bonding strength has always been a very active research field for composite materials. Compared to the overall composite materials, the proportion of interface is relatively small and complex, which results in a great difficulty in measuring the performance of a separate interface. The methods used to measure the interfacial strength of composites can be mainly divided into three categories: macroscopic test methods, mesoscopic interface test methods and micro-composite experimental methods, as shown in Table 1. The macroscopic test methods are focus on the macroscopic composite, such as 3D fabric carbon fiber reinforced resin composites, 2D carbon fiber composite board, etc. Macroscopic test methods mainly include 90° tensile, Off-axis tensile, Notched impact, Noel ring (NOL), Interfacial shear strength (IFSS), Scanning electron microscope (SEM), etc. Mesoscopic interface test methods can be used for the carbon fiber bundle composite and single fiber composite. Mesoscopic interface test methods include IFSS, SEM, atomic force microscope (AFM), X-ray photoelectron spectra (XPS) and Wetting characterization, etc. Micro
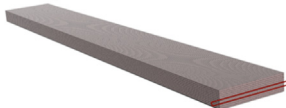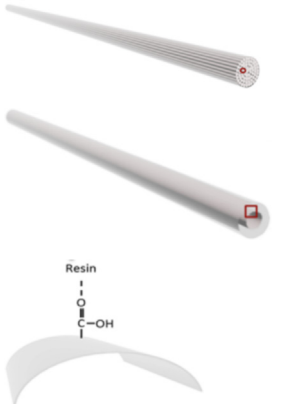
characterization methods focus on the micro fiber surface performance characterization which include SEM, AFM and XPS, etc.

Macroscopic test methods are used to evaluate the macro interfacial adhesion between fibers and polymer matrix. Some testing methods are put forward by Prosen and Chiao [4], such as short beam shear, off-axis tension and guide groove shear method. All of these methods are sensitive to the interfacial strength. The obtained results depend on the volume contents, distribution and nature of fibers and matrix. Pores and defects' content and distribution in composites also affect the results. Specially, these experiments damage the interface, matrix, even fibers. These methods have significance for composite material applications in engineering, i.e. the effect of interface modification can be quickly evaluated. However, they can be only used for qualitative comparison of the interfacial adhesion properties, not for the independent quantitative evaluation of the interfacial strength.

Characterization of microscopic composite material interface includes testing of micro-composites and in-situ characterization. Micro-composite material testing method is to measure the interfacial adhesion of micro-composite materials composed of resin and embedded monofilament fiber in matrix. Some methods, such as single-fiber pull-out, fragmentation, micro-debonding, proposed by Broutman and Cox [5], could directly measure the interfacial strength quantificationally or semi-quantificationally. Some experimental data have been used in composite materials design and life estimation, but the complexity of the sample preparation, experimental technology, and model simplification make the measured values of interfacial strength quite different via various methods.

Micro-debonding testing is an in-situ characterization method of interfacial adhesion, which can be directly carried out on the actual composites. The basic principle is to add an axial pressure on a selected individual fiber of composites by a diamond probe with the help of an optical microscope and precise positioning mechanism. When interfacial debonding occurs between the fiber and surrounding matrix, the axial pressure is obtained, and the resulting interfacial shear strength is calculated through finite element method based on the micro model. The samples used in this method can be directly cut from the actual composites, without special preparation. The measured results can not only be used to evaluate the performance of composite material products, but also

Table 1
Schematic diagram of interface adhesion characterization.

Macroscopic test methods		90° tensile Off-axis tensile Notched impact NOL ILSS SEM
Mesoscopic interface test methods		IFSS SEM AFM Wetting characterization
		IFSS SEM AFM XPS Wetting characterization
Microscopic experimental methods	Resin | O || C—OH	SEM AFM XPS

to detect performance in the course of usage at any time, it is a very promising approach.

In addition, another micro characterization technology which can be used to evaluate interfacial stress was developed by R.J.Young [6]. Stress distribution and stress transfer of carbon fiber reinforced composite material can be measured by using Raman spectrum, in terms of the linear relationship between the frequency shift of Raman spectrum and fiber strain. Cooperating with this technology, stress distribution of composite materials can be deeply comprehended.

Recently, a model with three parameters is proposed, which can relate the interfacial binding energy, interfacial micro-adhesion and the macro performance of CFRP. In this model, adhesive strength (τ) of the composite material with different contact area (s) is determined. When $s \rightarrow \infty$, with the increase of contact area, adhesive strength will tend to be a constant and can represent interlaminar shear strength of the two layers of the composite material. When $s \rightarrow 0$, adhesive strength can be considered to be the interface shear strength between fiber and resin. The model with three undetermined parameter is shown in Equation (1).

$$\tau = A + Be^{-\lambda s} \tag{1}$$

In which, A, B and λ are three undetermined constants which are related to the composition of composite material and interfacial tension.

The preparation of the testing composites is shown as Fig. 1. With this method, the relationship between microscopic interfacial strength and macroscopic properties of composite materials can be revealed, as shown in Fig. 1.

1.2. Interfacial residual stress characterization of FRP

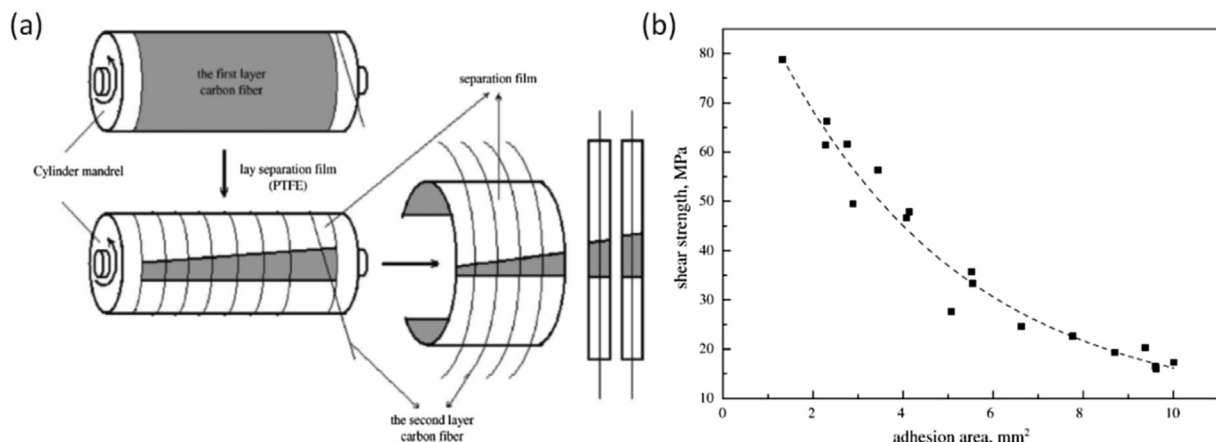Residual stress in carbon fiber laminates will cause premature

Fig. 1. (a) Process of producing meso composites specimen. (b), Relationship between shear stress and adhesion area.

failure upon tensile loading. If it is large enough, it will cause ply failure even in the absence of applied stress. Many factors aid in the formation of the process-induced residual stresses, such as chemical shrinkage caused by polymer crosslinking, thermal property mismatch, and overall anisotropy of composite materials.

X-ray diffraction technique was developed and applied to determine the interfacial residual stress of CFRP [7]. Carbon fiber is graphite-like structure, consisted of many graphitic lamellar ribbons oriented roughly parallel to the fibers axis with crystallinity more than 80%. The residual stress at the CFRP interface makes the crystal plane spacing of carbon fiber change, which can be detected by analyzing X-ray diffraction peak.

According to the Bragg diffraction equation $2d\sin\theta=\lambda$ [8], the measured diffraction angles 2θ can be used to calculate the crystal plane spacing, by which strain stress can be calculated according to the theory of elastic mechanics. It can be assumed the residual stress applied on carbon fiber as a way of axial symmetry, due to its lager length-diameter ratio of carbon fiber.

Assuming that carbon fiber axial is Z, when the measuring direction is perpendicular to the fibers axis, the strain (ε_z) of carbon fiber in Z direction can be obtained from the diffraction peak shift.

$$\varepsilon_Z = \frac{d_Z - d_Z^0}{d_Z^0} \qquad (2)$$

Where d_Z is the crystal plane spacing perpendicular to the fiber axis, d_Z^0 is the crystal plane spacing without stress (measured by free carbon fiber).

When measuring the crystal diffraction parallel to the direction of carbon fiber axis, ε_r is the measured strain.

$$\varepsilon_r = \frac{d_r - d_r^0}{d_r^0} \qquad (3)$$

According to Equations (2) and (3), the axial and radial strain of carbon fibers can be calculated.

It can be assumed that direction Z and direction R are the main direction of stress, so that,

$$\sigma_Z = \frac{E_Z[2v_{rZ}\varepsilon_r + (1 - v_{r0})E_Z]}{1 - v_{r0} - 2v_{rZ}v_{Zr}} \qquad (4)$$

$$\sigma_r = \frac{E_r(\varepsilon_r + \varepsilon_Z v_{Zr})}{1 - v_{r0} - 2v_{rZ}v_{Zr}} \qquad (5)$$

Where E is the elastic modulus of carbon fiber, υ is the Poissson ratio of carbon fiber, the residual stress in the axial (σ_z) and radial direction (σ_r) of the carbon fiber/matrix interface can be obtained.

Using this method, the interfacial stress of carbon fiber/epoxy with expansion monomer can be obtained [9], as shown in Fig. 2. As the bulk effect caused by expending monomer overcomes the problem of epoxy resin volume shrinkage during solidification essentially, introducing it reduces the residual stress of CFRP interface.

1.3. Characterization of the interfacial chemical composition and interfacial phase characteristics

The characterization of interfacial chemical structure mainly refers to analysis for constituent elements, valence, and their distribution of interface, which is often analyzed with traditional spectrum, such as infrared spectrum (IR), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), election probe, secondary ion mass spectrometer (SIMS), electron energy loss spectroscopy (EELS), micro Raman spectroscopy (MRS),
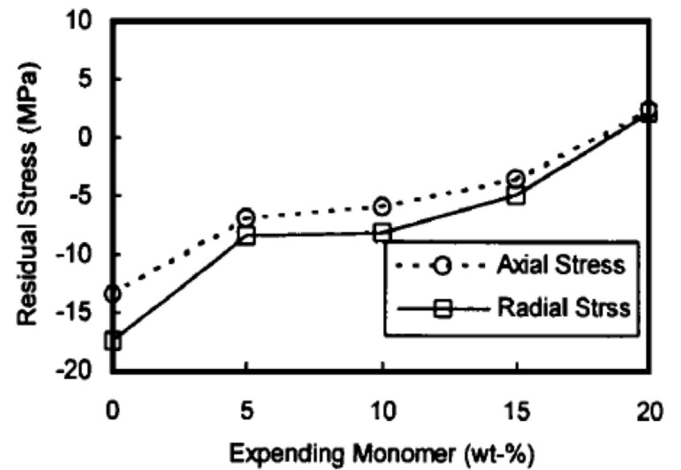

Fig. 2. Residual stress of composite material with different expending monomer wt%.

extended X-ray absorption fine structure spectroscopy (E-XAFS) and so on. The methods, using spectroscopy to characterize interface chemical composition, have been reviewed in some articles [10]. Although these methods are widely applied, they have many kinds of limitations. For example, the analyzed interface is often required to be stripped, meanwhile, the interface size is much smaller than some of the beam spots. In addition, some methods can only provide element information but can't acknowledge element valence states, etc.

The characterization technology of interface morphology and thickness includes transmission electron microscopy (TEM), scanning electron microscope (SEM), atomic force microscope (AFM), etc. These methods have great guiding significance in studying the interface uniformity, the interface transition layer, resin permeability and the selectivity of interface reaction.

1.4. Characterization on thickness, modulus of interphase between fibers and matrix and their distribution by AFM

AFM is a sensitive tool for characterizing surface properties of a series of material systems from soft polymer to rigid ceramic and metal [11]. Recently, in addition to conventional topographical imaging, several technologies based on AFM, have been developed to explore the interfacial properties of fibers reinforced composites, such as nanoindentation [12], force modulation mode [13,14] and phase imaging [15]. Among these technologies, force modulation AFM, which is widely used in polymers [16], semiconductors [17,18], biological [19,20], especially in composite materials investigations, is particularly useful for detecting soft and stiff areas on substrates which exhibit overall uniform topography [21].

The force modulation AFM allows a qualitative statement about the local modulus of sample surface using an oscillating cantilever tip which indents into the sample surface. In accordance with the local modulus of the sample, corresponding cantilever amplitude will change under scanning. On the stiff areas of the sample surface, the depth of indentation will be smaller, and on the compliant areas, it will be larger. So the different responses of the cantilever from areas with different modulus can be observed.

The force modulation images obtained from the cross-section of the fine polished carbon fiber reinforced epoxy composites are shown in Fig. 3. In a force modulation AFM image, the different color contrasts are corresponding to different modulus. The interphase region captured from untreated carbon fiber composites is shown in Fig. 3a. The thickness of the interphase is very
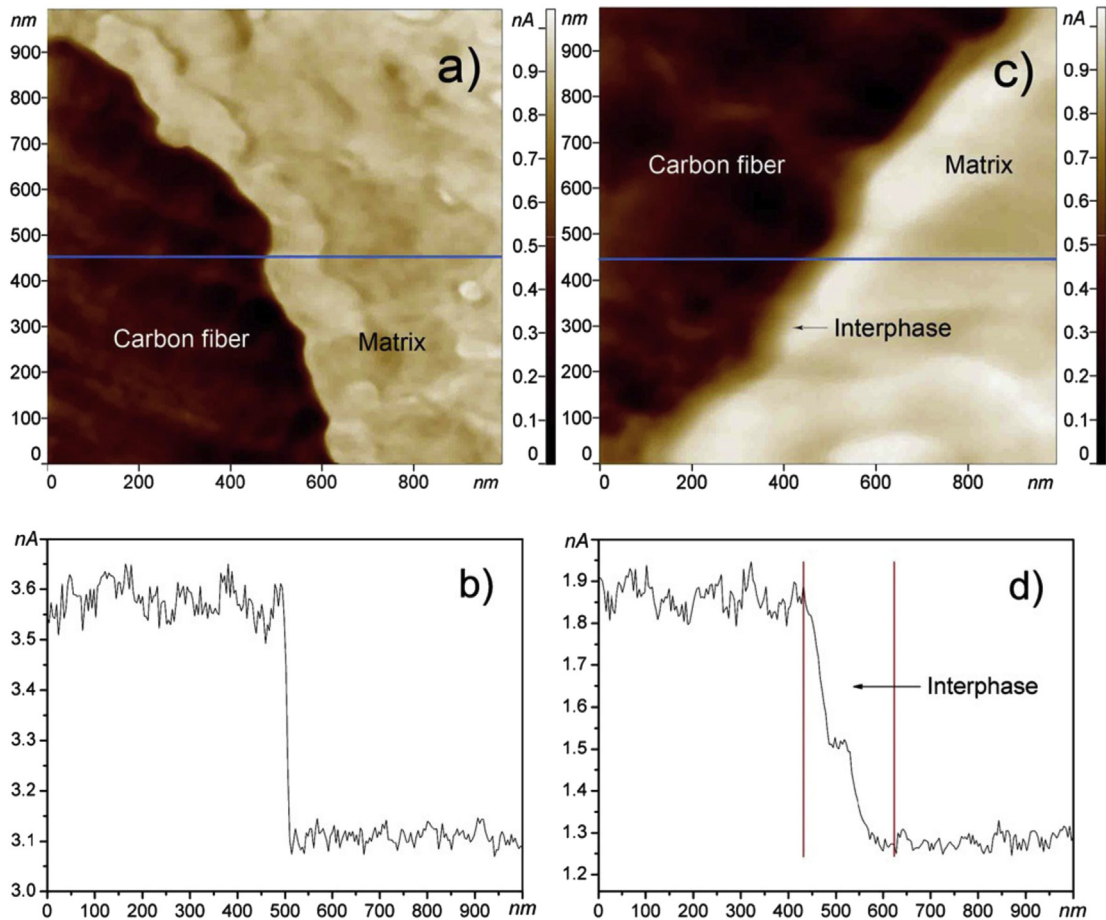
Fig. 3. Force modulation AFM images of composite interphase region. (a) phase image for untreated carbon fiber composite. (b) line profile for a (blue line). (c) phase image for treated carbon fiber composite. (d) line profile for c (blue line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

small and the modulus sharply changes from the carbon fiber to the matrix. The crosslink of the matrix is not affected by the fibers surface. Compared with the untreated composites, an obvious interphase with a thickness of 100 nm exists in the modified carbon fiber composites. And obvious contrast among the fibers, interphase and matrix region reveals a difference in the visco-elastic property of these three regions. From the section analysis image (shown as Fig. 3), it also can be obviously observed that a distinct modulus transition region exists corresponding to the interphase.

1.5. Characterization on the distribution of surface coating of fibers and the diffusion between resin and sizing of fibers

Sizing is a part of carbon fiber and must provide a new set of properties to optimize composite processing and performance. Unfortunately, it has been found that the distribution of the applied sizing layer is frequently non-uniform. Thomson and D.W. Dwight [22,23] analyzed the XPS data from a wide range of commercial and experimental glass fibers and present a glass-fibers' sizing characterization model, based on a patchy sizing overlayer hypothesis, shown as Fig. 4.

For glass fibers coated with organic materials (at C/Si > 10), silicon could be used as a characteristic atom for the glass with negligible loss of accuracy in the analysis. They developed a protocol to plot the ratios of appropriate atom concentrations and established the relationship between C/Si data of glass fibers from

XPS and coverage of sizing from LOI by fixing the curves. And they estimated the surface coverage of the sizing on glass fibers to obtain information on the stoichiometry of the sizing. Using this model, XPS results, combined with the weight fraction of the sizing, gave a quantitative value for the coverage of the fibers' surface by the sizing.

According to D.W. Dwight's model, it is important to determine the atoms which are characteristic only of the sizing or the fibers for carbon fiber. Carbon, oxygen and nitrogen are present in both sizing and fibers, so it is difficult to select a kind of atom as signal exclusive to the carbon fiber' surface layer. In our investigation of carbon sizing, the brominated epoxy resin was added to the carbon fiber sizing. Combined with the Dwight's model, the bromine can be used as the characteristic atom and the sizing layer can be analyzed to provide the information used to predict and control their influence on processability and composite performance.

For interface characterization, it is common that one characterization specificities in analyzing one interfacial property. For example, interfacial chemical composition and distribution only apply to analysis of interfacial reaction. The analysis of the interface transition layer's thickness and modulus can be used to analyze the infiltration characteristics of interface, and so on. These methods are used to prove that the carbon fiber surface modification and the effect of the resin modification are helpful to establish the relationship between the microscopic interface properties and the macro mechanical properties. Interface characterization faces great difficulty, because there is a certain distribution in composite
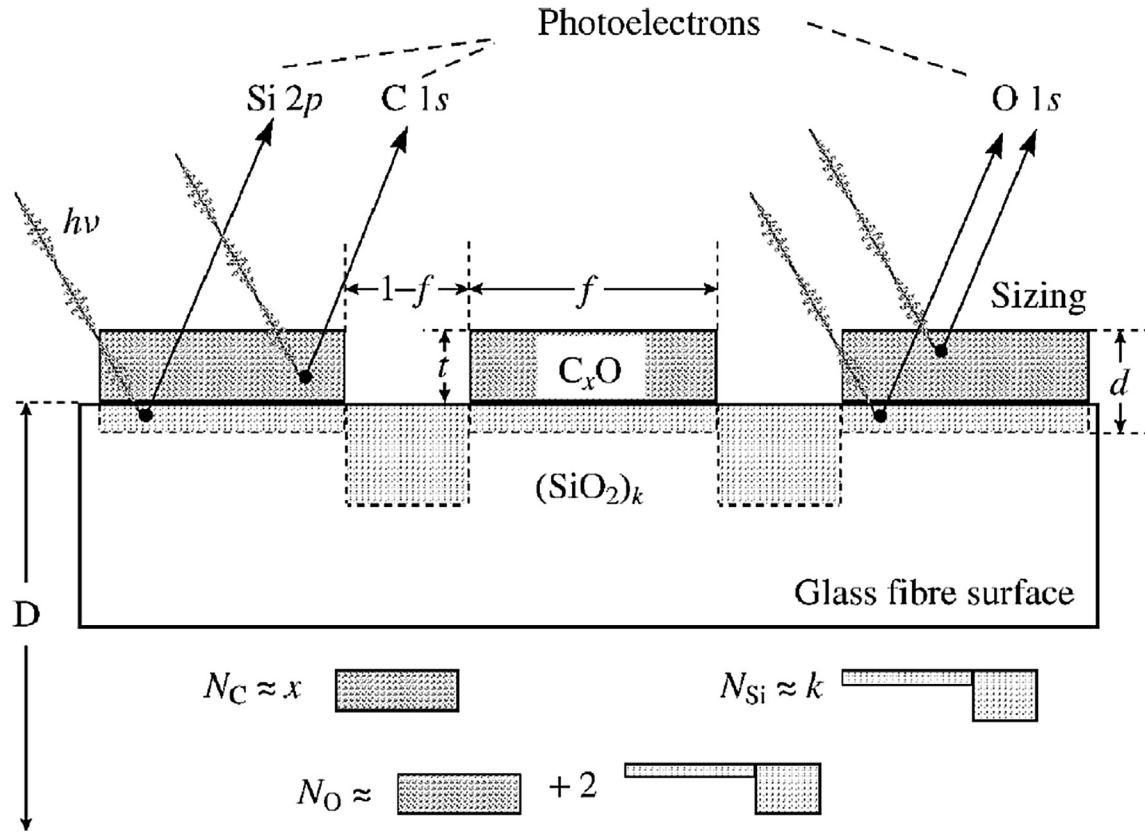
Fig. 4. Schematic diagram of the cross section of a glass fibers with an idealized sizing distribution.

material and a dispersion in interfacial physical and chemical properties. Judging from the current situation, although there are lots of problems, researches for composite material interface characterization continue being developed toward a more microscopic and more quantitative direction. Interfacial characterization is helpful to the engineering application of composite materials and micro interface mechanism research, especially for designing of novel composite material, such as a new generation of high performance composite materials consisted of micro-nano scale materials, dendritic compound materials, etc. The research on interface impact has been developed from the initial studies on modifying the hydrophilic and lipophilicity of fibers or resin to more microscopic micro-nano scale design and control. Thus, the in-depth study on infiltration characteristics, reaction features, and interface stress transfer characteristics has become the important trend in the field of composite material, at present.

2. Interfacial control of CFRP

Interfacial control of CFRP mainly focuses on forming a control and stable surface structure on CF, and effective modeling. It is also focused on that ordering interphase to understand the interfacial mechanism and establishing the industrial control method based on the interfacial mechanism.

In the process of CFRP, the matrix resin will wet the carbon fiber and resin is adsorbed on the surface of CF to form the interphase of CFRP. The interfacial control can be obtained through the changing of the surface feature and resin component to adjust the wettability between CF and resin. The molecular assembly can be a method to control the interface structure according to the design. But on the other hand, the resin used is usually the multi-components polymer, such as epoxy system including the epoxy resin, curing agent

and other modification agent. The adsorption behavior of different components will influence the interphase of CFRP, especially for the matrix resin with organic solvent. This paper introduced the control of CFRP from two aspects.

2.1. Molecular assembly of carbon fiber and molecular dynamic simulation

Molecular self-assembly provides a means to obtain a controlled and ordered structure. Self-assembly monolayers (SAMs) are usually prepared. In solutions, organic molecules spontaneously chemisorbed on solid substrates with a strong coordinative bond via sulfur atom, and they formed a closely packed and highly ordered monolayers by the van der Waals interaction among the molecules. Although self-assembly monolayers (SAMs) systems have occupied a wide range of applications in the fields of biology, microelectronics, optics and coatings, its studies in composite systems have been seldom reported. Lu et al. [24] have investigated the organic heterocyclic compounds containing nitrogen or sulfur atoms as self-assembly thin films in aluminum powder/polyurethane composites in detail. They found the treated aluminum powder-reinforced PU composites possessed a higher tensile strength and higher elongation than those of the untreated systems. As far as we know, no studies concerning SAMs at carbon fiber/epoxy interface have been considered so far.

He JM [25,26] et al. developed a new method based on molecular-assembly on CF surfaces to obtain a controlled interface between carbon fiber and epoxy matrix in composite system. The surfaces of carbon fibers were first metallized by electroless Ag plating; then they were reacted with a series of thiols with different chain lengths and terminally functional groups to form self-assembly monolayers (SAMs), which further reacted with epoxy

resin to generate a strong adhesion interface. They chose alkanethiols with different alkyl chain lengths and aromatic thiols with different terminally functional groups to control the interfacial thickness and change the interfacial properties. The results of SERS and XPS analysis revealed these organicsulfur compounds chemisorbed onto the Ag-coated carbon fiber's surface through the formation of Ag-thiolates. In terms of SERS selection rules, it could be concluded that the alkyl chains of alkanethiols SAMs were vertical to the Ag/carbon fiber surface, whereas the benzene rings of aromatic SAMs were parallel to the surface. The interfacial shear strength (IFSS) from the microbond testing of the composites increased reinforced by treated carbon fibers with alkanethiol SAMs. This was due to the organic molecules oriented perpendicullarly on the Ag/carbon fiber surface acted as coupling agents by the interaction of hydroxyl and epoxy groups to generate the strong adhesion interface. Moreover, the longer the chain was, the higher the IFSS was. This is because the longer alkyl chain molecules formed a more closely packed structure with more active functional groups exposed at the outermost surface. The IFSS of the treated carbon fibers composites with aromatic thiol SAMs also increased. It can be concluded that the effects of functional groups on the interfacial properties were strong, due to the higher reactivity of $-NH_2$ groups toward the epoxy than that of $-OH$ groups.

The interface structure between the self-assembled monolayers on Au (111) surface and epoxy resin was researched by molecular dynamics methods [27]. The influence of the chain length and the end groups of the SAMs on the interfacial stability was discussed through the interface interaction energy. The simulation results were verified by experiments, which proved that the simulation method was advisable. The simulations indicated that: for $HS(CH_2)_nOH$, the interface interaction energy was the lowest when n is 11, and for $HS(C_6H_4)X$, the energy was the lowest when X is $-COOH$ (as shown in Fig. 5).

2.2. Competitive adsorption of resin on the fibers surface and its control

The solution impregnation route is often employed to fabricate polymer-based composites through resin transfer molding (RTM) process. It is necessary to use organic solvents to easily wet-out the reinforcement for some high viscosity resins such as phenolics. However, the adsorption of resin components is complicated, which is the result of interactions between reinforcement, solvent and polymer. The components of the resin solution are adsorbed onto the surface of the reinforcement and determined the overall performances of the ultimate product.

The adsorption of phenolic resin onto silica fibers was investigated through selection of solvents with different hydrogen bond donor ability. It has been proved that the interaction between phenolics solute and solvent plays an important role in control the adsorption of solute on a silica fibers surface. Hydroxyls and hydroxymethyls of phenolic resin will form intermolecular hydrogen bonds with the solvents used. These intermolecular hydrogen bonds in solution compete with the intermolecular (i.e., adsorptive) hydrogen bonding with the silica surface. The stronger the hydrogen-bonding interaction in the solution is the less the adsorption of phenolic resin on the fibers surface has. So phenolic resin adsorption was suppressed significantly because of the competitive adsorption of solvent onto silica substrate and strong solvent–solute interaction.

The competitive adsorption was also investigated by carbon fiber modification by silane agent with different organic functional groups. Silane species present fibers surfaces with different polarity by possessing different hydrogen bonding abilities and different residue silanol group contents on silica fibers surface. Wang B.C. et al. [28–32] analyzed the surface polarity of carbon fiber and found that it contributed to the competitive adsorption, as shown in Fig. 6. Silica fibers with amino groups silane agent was proved that the protonated amino groups are developed through hydrogen-bond interactions. It led to the improvement of mechanical interfacial properties of silica fibers/phenolics composites, and it decreased inhomogeneities of resin distribution and mechanical interfacial properties at different regions of the RTM products.

Finally it was proved that the competive adsorption of phenolics components onto silica fibers was the result of hydrogen-bonding interactions among reinforcement, solvent and polymer. The adsorption of phenolics onto silica fibers was consistent with Langmuir isotherm.
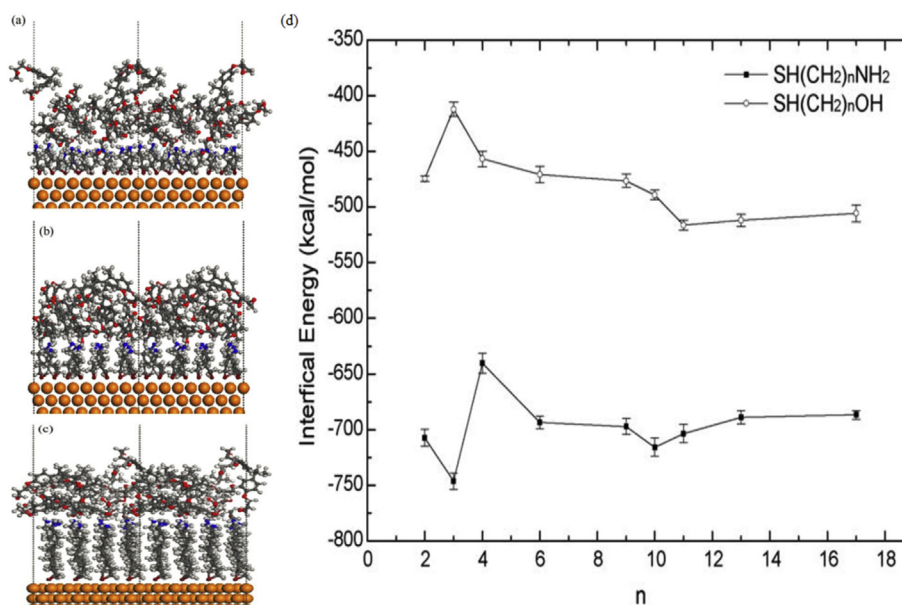

Fig. 5. The interface structures and results of the $S(CH_2)nNH_2/Au(111)$ and epoxy resin. (a) $S(CH_2)_3NH_2$. (b) $S(CH_2)_4NH_2$ and (c) $S(CH_2)_{10}NH_2$. (d) Comparison of the interface energies of two different types of SAMs/Au(1 1 1) and epoxy interface.
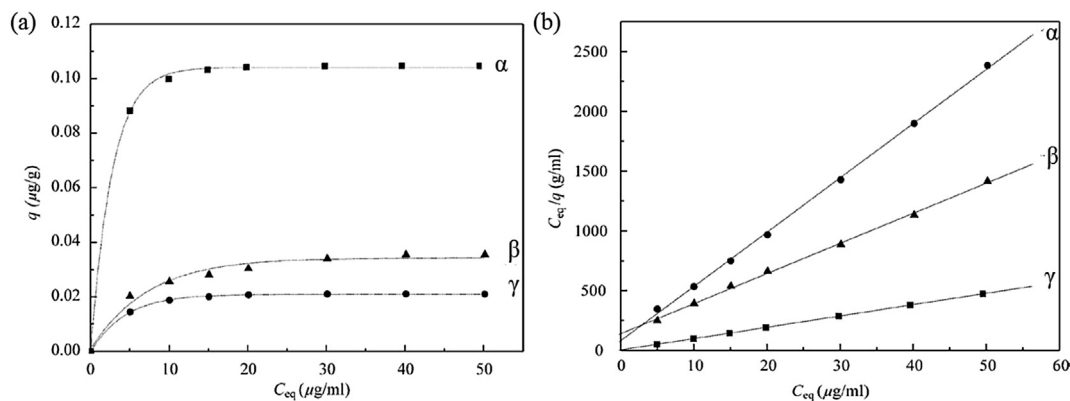
Fig. 6. (a) Adsorption isotherms for phenolic resin onto silica from different solvents. α. Dioxane; β. DMF; γ. ethanol. (b) C_{eq}/q as a function of equilibrium concentration of phenolic resin in different solvents, C_{eq}. α. Ethanol; β. DMF; γ. dioxane.

3. Interfacial modification of CFRP

The carbon fiber surface modifications, with which fiber performance and fiber reinforced materials composite are all improved, have been widely used for carbon fiber related material fields, such as carbon fiber fabrication, carbon fiber reinforced materials. The modification methods can be divided into two types: oxidation and non-oxidation.

Oxidation is the method with using an oxidizing agent to improve the activity of functional groups on the carbon fiber surface. Promoting the physical and chemical reactions between the fibers and resin by oxidation in order to improve the interface performance of the composite materials. Oxidation includes gas phase oxidation carried in air, oxygen or ozone, liquid phase oxidation with nitric acid & sulfuric acid, ammonia, hydrogen peroxide, sodium hydroxide, potassium permanganate, chlorate, hypochlorite, persulfate as the oxidant, anodic oxidation carried with sodium hydroxide, ammonium bicarbonate, sulfuric acid, nitric acid, ammonium nitrate and organic acid or the salts of organic acids as electrolyte.

Non-oxidation is the method, with which the infiltration and interfacial reactivity of the resin to the carbon fiber can be enhanced to improve the interfacial performance of the composite materials. The structure and surface energy of the carbon fiber surface was regulated with coating, grafting, cleaning, etching and so on. With these methods, such as plasma, chemical grafting, surface cleaning, the weak layer of the carbon fiber interface can be removed to some degree, and the surface roughness of the carbon fibers and the engagement of the interface can be improved. Meanwhile, the surface energy of the carbon fiber will increase, so that the interface infiltration effect can be improved. Fibers surface functional groups will increase to promote the interfacial reactions.

Interfacial properties of carbon fiber reinforced composites can be promoted to modify the resin, through changing surface tension of the resin system, increasing the infiltration of resin to fibers and improving the mechanical properties of the resin itself.

3.1. Surface cleaning and activation of carbon fiber by supercritical or subcritical fluids

Generally, cleaning the sizing of carbon fiber is the first step for the research on the surface modification of CF, such as acetone Soxhlet extraction and burning under inert atmosphere [33,34]. But it is difficult for extraction to remove wholly the sizing of CF, and burning method will decrease the tensile strength of CF.

Carbon fibers can be cleaned by supercritical water, supercritical acetone and subcritical potassium hydroxide aqueous solution

[35]. Supercritical fluid has both liquid-like and gas-like characteristics, such as density between the two states, high diffusivity and good heat-transporting properties. From this point of view, supercritical fluid is a medium with excellent transport property. The effect of cleaning temperature and duration time were investigated, and experimental results revealed that the method of using these three fluids to act as the processing mediums showed a better cleaning result compared to the traditional method, Soxhlet extraction with acetone. In addition, using supercritical acetone or subcritical potassium hydroxide aqueous solution acted as cleaning medium is more efficient than Soxhlet extraction with acetone. For the method using supercritical acetone, it leads to less damage to each kind of carbon fibers after treated, and it is particularly appropriate for removing epoxy resin coating layers on the surfaces of carbon fibers. Comparatively, cleaning with subcritical potassium hydroxide aqueous solution may cause more serious losses of single filament strength to the cleaned fibers, but using this method can remove silicious contaminants thoroughly for the cleaned carbon fibers.

In order to improve the interfacial properties between carbon fibers and epoxy matrix, supercritical water and hydrogen peroxide were used as oxidation medium in the oxidation treatment for carbon fibers [36,37]. The experiment results showed that the amount of oxygen functional groups on the surfaces of carbon fibers increased after treatment, and the majority of these groups were carboxyls. Meanwhile the surface appearance of the treated carbon fibers was significantly affected by the oxidation reaction in supercritical water [38]. This peculiarity was attributed to the particular physical characteristics of the supercritical fluid, such as high penetrability and density fluctuation.

As the method mentioned above, in our previous works [36], we used supercritical water and hydrogen peroxide to treat carbon fibers surfaces. After the treatment the interracial banding between carbon fibers and epoxy matrix were enhanced by this method, in terms of IFSS and ILSS tests results. The reason is the roughness of the fiber surface was improved with the content of H_2O_2 increased as shown in Fig. 7(a–e) and the roughness was also increased with the increase of oxygen functional groups on the surfaces of carbon fibers as the XPS results showed in Fig. 7f, and main of them are carboxyls. At the same time, the tensile strength hardly changed after the treatment.

For the purpose of the activation of carbon fiber, $KMnO_4$/subcritical water, $KMnO_4/Br_2$/subcritical water and concentrated sulfuric acid/supercritical Br_2 oxidation systems were designed [39,40]. The causes for designing such a mixed oxidation system included three aspects: firstly, the $KMnO_4$ used in the oxidation
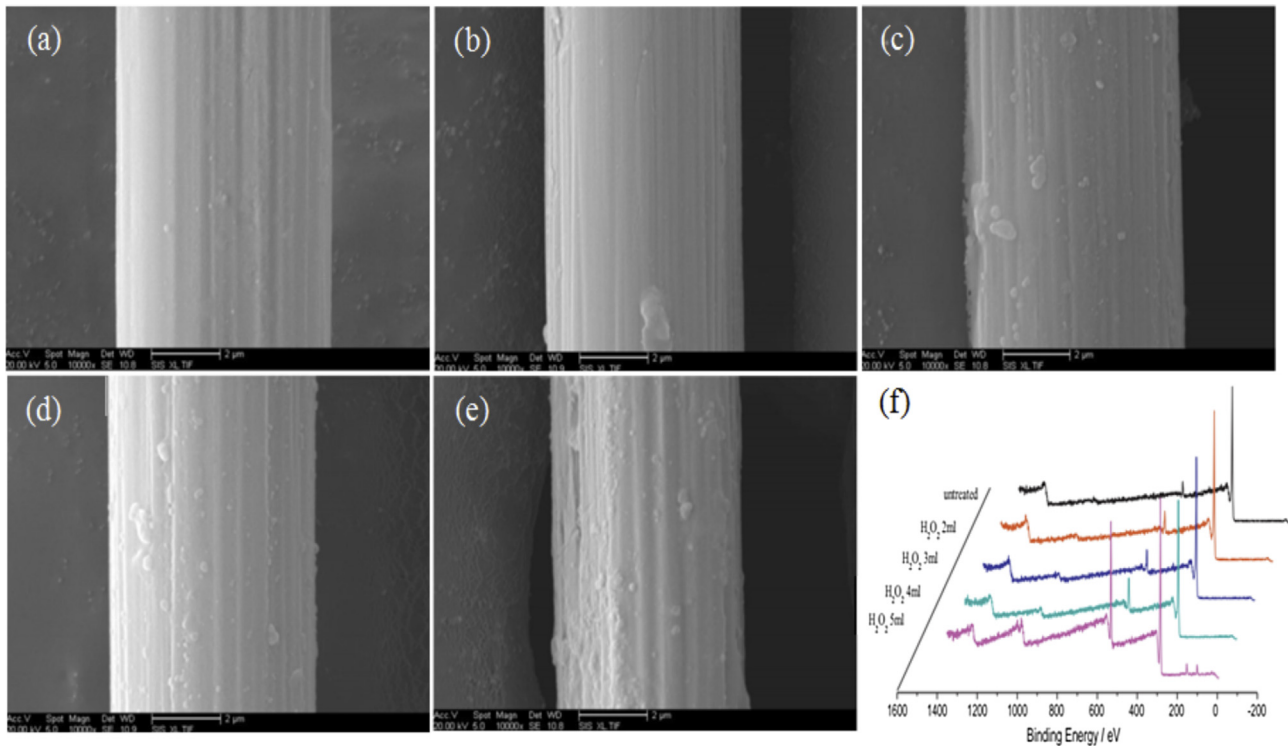
Fig. 7. SEM photos (×10,000) of carbon fibers' surfaces treated with various conditions (a) untreated. (b) 2 mL H_2O_2. (c) 3 mL H_2O_2. (d)4 mL H_2O_2. (e) 5 mL H_2O_2. (f) survey spectrum of XPS analyses for treated and untreated carbon fibers [36].

system had a strong chemical activity, and it could oxidize carbon fiber surfaces efficiently; secondly, the Br_2 used in the system had a weak oxidability, and it did not react with the C atom on the surface of carbon fiber even under the condition of high temperature; lastly, when the C—C bonds in the surface structures were destroyed by the strong oxidant ($KMnO_4$) in the oxidation system, the Br_2 could react with the fiber surfaces through free radical reaction or substitution reaction. Because the concentration of Br_2 was much higher than the concentration of $KMnO_4$, the presence of Br_2 had a marked effect on the properties of this oxidation system. It showed that the oxygen content of carbon fibers increased significantly after treated in $KMnO_4$/subcritical water. The oxygen content on fiber surfaces increased, after proper amount of Br_2 was mixed into $KMnO_4$/subcritical water in the oxidation, but the main generating group was hydroxy not carboxyl. Such phenomenon also appeared with concentrated sulfuric acid/supercritical Br_2 oxidation systems. It showed that, as a feature of these oxidation treatments, hydroxys are the main oxygen-containing groups generating on the treated fiber surfaces.

3.2. Surface treatment of carbon fiber by anodization

Since most carbon fibers are utilized as reinforcement with resin matrix, their surfaces are oxidized in order to obtain adequate adhesion between the fibers and resins. The most practical surface treatment for commercial production of carbon fiber is anodization, because the level of surface oxidation is easy to control [41,42].

The anodic oxidation of carbon materials in aqueous electrolyte solutions is characterized by the concurrence between three reaction mechanisms: intercalation reactions, degradation of the carbon material (formation of colloidal and gaseous oxidation products) and formation of covalently bonded surface groups. The reaction mechanism was influenced by the kind and concentration of the electrolyte system and the electrolysis conditions. Many researchers have reported changes in surface chemical structures of carbon fibers through the anodic oxidation treatment.

Denison et al. proposed a model of the surface oxidation mechanism for PAN-based carbon fibers which had intercrystallite voids on the untreated surface. Through oxidation, the original surface was consumed, and new surfaces and edges appeared. Additionally, the intercrystallite voids became wider [43]. Fitzer and Rensh had reported that the ILSS varied considerably depending on the kind of electrolyte. Ehrburger and Donnet found a good correlation between the number of carboxylic acid groups and ILSS through anodization in HNO_3 and NaOH. Moreover, Fukunaga et al. [44] found a strong correlation between the double layer capacity and ILSS values. The mechanism of anodic oxidation for pitch-based carbon fibers is proposed to be selective oxidation and the appearance of prismatic surfaces in crevices. Since the prismatic surfaces have many sites that are chemically active to epoxy resin. Pitch-based carbon fibers show a strong adhesion between the fiber and the resin even after the fiber has been deoxidized (as shown in Fig. 8 a–b). In addition, Qian [45] discovered that electrochemical anodic oxidation treatment in ammonium–salt solutions could increase the root mean square roughness of carbon fibers with the largest extent from 4.6 nm to 15.7 nm. The relative content of polar elements such as oxygen and nitrogen also increased after surface treatment. There was an extensive improvement in ILSS values of carbon fibers after electrochemical oxidation treatment (as shown in Fig. 8 c–f), whereas the tensile strength of treated carbon fibers decreased obviously. When $(NH_4)_3PO_4$ was taken as the electrolyte, the chemical reaction on carbon fibers surface was violent and its damage to the properties of carbon fibers was greatest severity. There was a direct correlation between chemical reaction intensity and the concentration of OH− ions in ammonium–salt electrolytes, and the higher the concentration of OH− ions in the electrolytes was, the more violently the oxidative reaction happened.
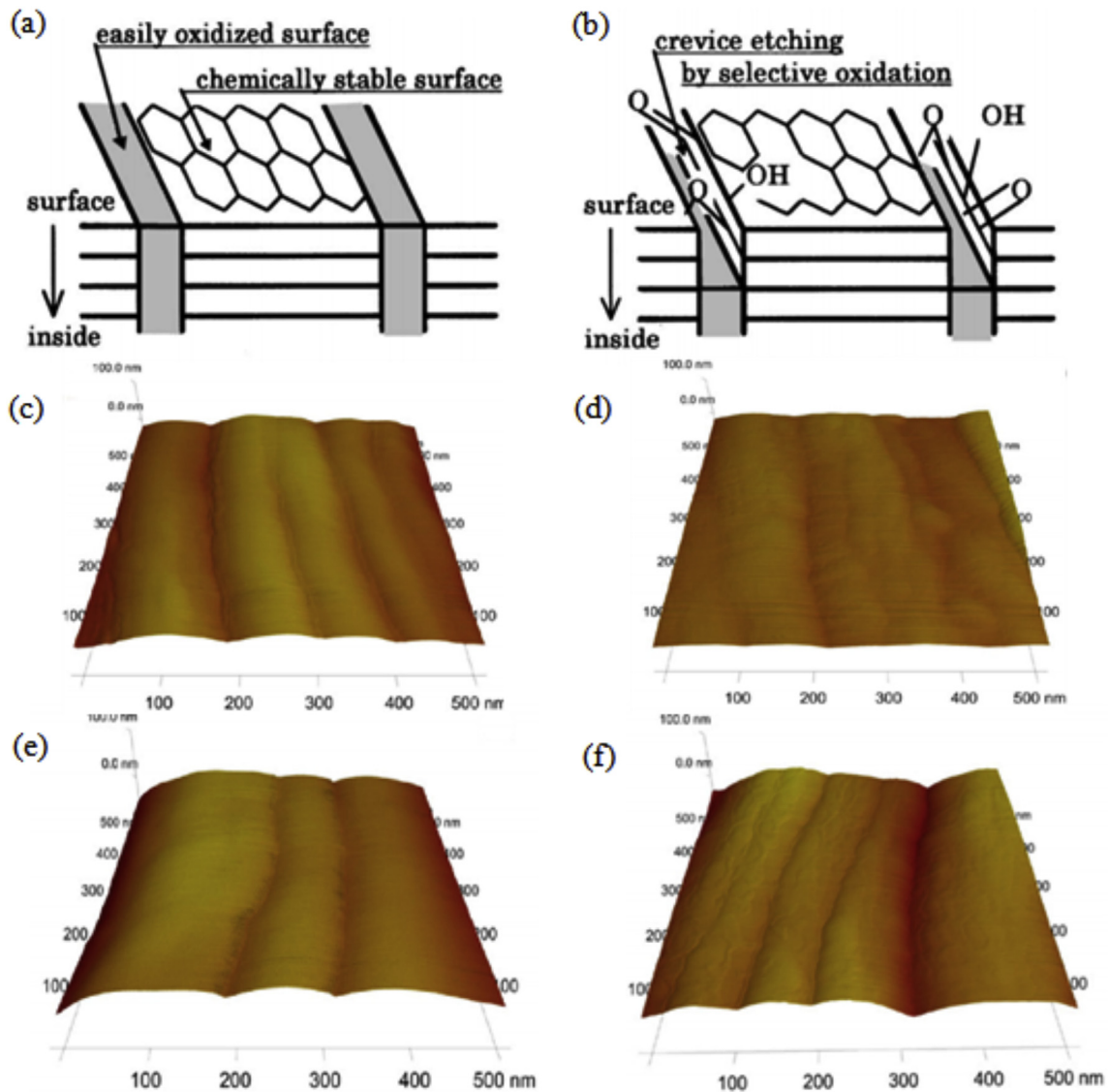
Fig. 8. Schematic models for the mechanism of surface oxidation of pitch-based carbon fiber: (a) before anodic oxidation. (b) after anodic oxidation. (c–f) Surface AFM images of carbon fibers: (c) untreated. (d) Treated NH_4HCO_3. (e) Treated $(NH_4)_2CO_3$. (f) Treated $(NH_4)_3PO_4$ [44].

3.3. Surface modification of carbon fiber by plasma method and irradiation method

Plasma treatment is frequently used to modify carbon fiber surfaces to improve adhesion of the fiber to polymer matrix. Today, plasma modification has been used in many industrial applications filed to enhance the adhesion, improve bonding in polymer matrix composites.

So far, many researchers have reported changes in surface chemical and physical structures of carbon fibers through the plasma treatment. Among them, Qiu et al. [46] used the He/O_2 plasma to treat the carbon fibers surface to investigate the interface performance (as shown in Fig. 9a). They discovered that the plasma treatments can roughen the fiber surfaces (Fig. 9b–e). And dynamic water contact angles of the carbon fibers decreased with the treatment time increased. They presented that it was the main reason to increase the IFSS between the carbon fiber and PI. Rhee et al. [47] also found the similar result when they used the plasma to treat the carbon fiber surfaces.

Gamma radiation, also known as gamma rays and denoted by

the Greek letter γ, refers to electromagnetic radiation of extremely high frequency and high energy per photon. An irradiation can induce chemical reaction at any temperature in the solid, liquid and gas phase without any catalyst [48,49]. It is a safe method by which people can protect the environment against pollution, reduce maintenance cost and save energy consumption. In addition, γ-ray has high penetration depth to various objects and it can lead to a uniform distribution of radical initiating sites through the thickness of the irradiated samples, without considering the shape and volume, which is convenient for industrialization of CF.

There are essentially two basic methods for radiation grafting of CF: co-irradiation method and pre-irradiation method.

(1) Co-irradiation grafting method [50].

Co-irradiation grafting method is also called simultaneous grafting method. First, the carbon fiber and grafting monomer are mixed up in the same system, and then the whole system is irradiated under gamma ray condition after full contact (Fig. 10a). This method is easily operated, and the irradiation grafting process can
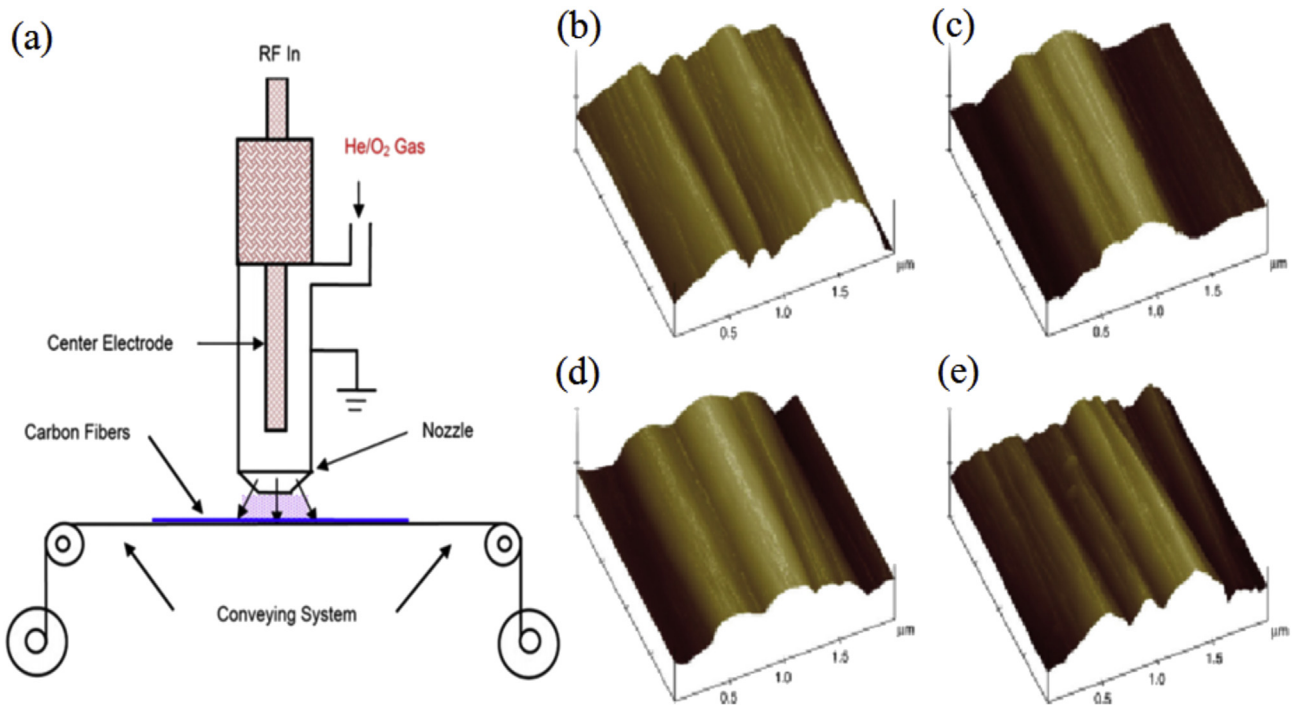
Fig. 9. (a). schematic of the atmospheric pressure plasma treatment system. (b−e) AFM micrographs of carbon fiber with different plasma treatment times. b control. c 16 s d 32 s and e 64 s [46].

be carried out simultaneously with the radiation process as shown in Fig. 10b.

In our previous work, we found that the ILSS of CF/epoxy composites enhanced about 37% after Co_{60} irradiation treatment. The performance improvement resulted from polar chemical bonds occurrence, such as−OH, −C=O and −COOH. Higher hydrophilic made a better wettability for epoxy composite processing. In addition, we also discovered that the excessive irradiation (>250 kGy) was not beneficial for mechanical interlocking between CF and epoxy resin, while the impregnating performance of CF was

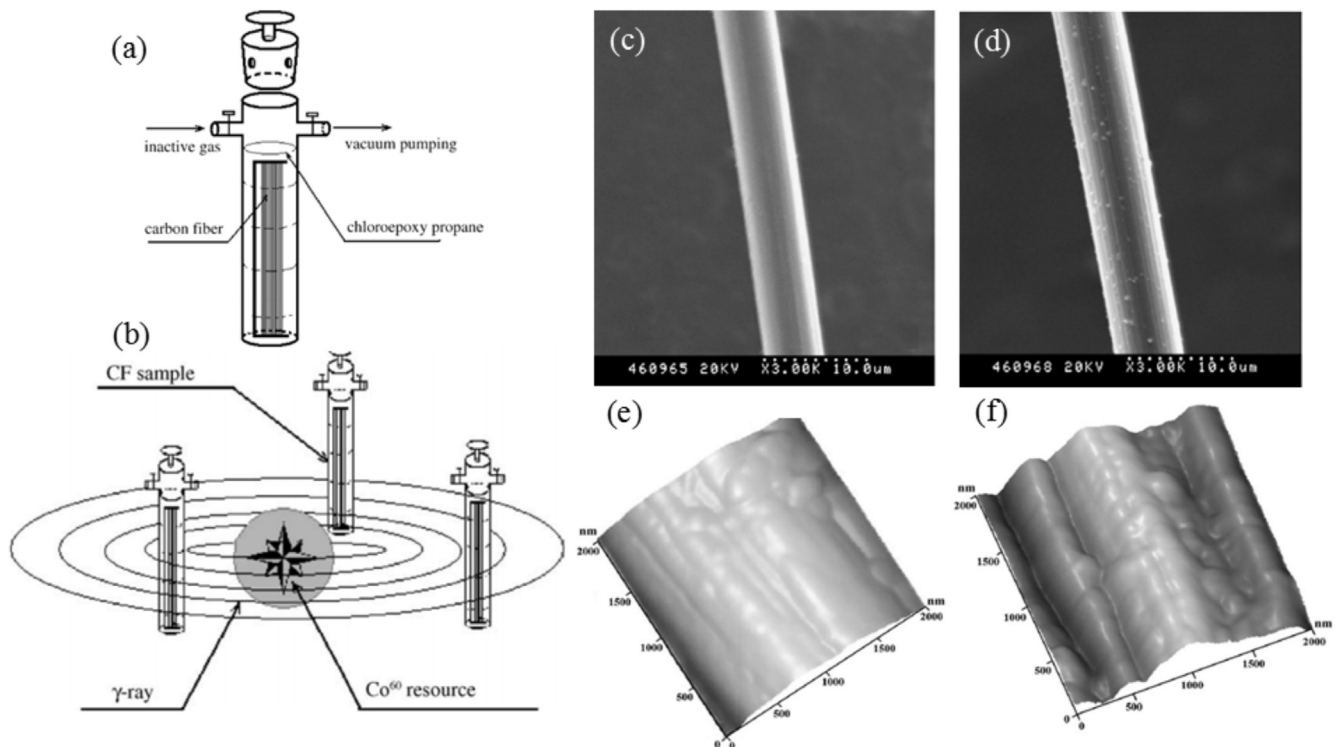**Fig. 10.** (a) Schematic of the irradiate instrument. (b) the schematic plan of CF irradiate process by a point-source Co60 radiator.(c−f). carbon fiber surface pictures of SEM and AFM: (c) and (e) untreated CF. (d) and (f) after irradiation [56].

improved after irradiation.

(2) Pre-irradiation grafting method [51].

In pre-irradiation, the carbon fibers are first exposed to Gamma-ray irradiation in vacuum or under inert atmosphere to generate radicals before being exposed to a grafting monomer. The irradiation is a step-wise with the grafting process, it can minimize the generation of homopolymer, but the efficiency of free-radical is relatively low during the grafting process.

Irradiation not only leads to CF intrinsic structural changes, resulting in the trench on the surface of CF, but also could link the functional monomer to CF via irradiated grafting method to improve its roughness. Thereby the smoothness and inert state of CF surface could be improved.

Gamma ray irradiation can also change the surface chemical composition of carbon fiber. For example, when carbon fiber was irradiated in the graft reagent chloroepoxypropane [52–56], the energy provided by gamma rays induced the active free radicals from both of CF and monomer. Then the grafting reaction occurred on CF surface, and the oxygen-containing groups from chloroepoxy propane were introduced onto the carbon fiber surface, which resulted in the oxygen content increase and carbon content relatively decrease. With the increase of irradiation dose, more groups with higher binding energy appeared gradually on the surface of CF. This result indicated that high energy of gamma ray could induce grafting reaction between CF and chloroepoxy propane, and it also could promote the conversion of groups with low binding energy to high binding energy in high irradiated dose.

In addition, some graft reagent monomers, e.g. chloroepoxy propane, has similar ingredient with epoxy resin matrix [57–59], which are more likely to react with resin matrix. The introduction of grafting agent molecular chain, via physical entanglement, formed the diffusion interface layer between the fibers and resin matrix, so that the loads can be spread more evenly along the interface, which is conducive to improve the interfacial properties of composite materials, shown as Fig. 10(c–f).

Besides above analysis, in recent, Xu et al. [55] investigated the effects of fiber instinct structure and radiation medium on surface modification of CFs in gamma-ray irradiation for T300, T400, T700, T800 and T1000, respectively. They presented that the changes of surface graphitization and roughness depended on the fiber instinct structure after irradiation. The graphitization of T300, T400 and T800 with low graphitization and rough surface increased after irradiation, while that of T700 and T1000 with high graphite degree and smooth surface decreased. Specific surface areas of low-graphitization CFs (T300, T400 and T800) were changed clearly, while those of high graphitization CFs (T700 and T1000) remained almost unchanged after irradiation. They also found that the surface chemistry changed after irradiation was determined by the type of the irradiation medium. The oxygen ratio of CFs irradiated in Ar decreased, while that of CFs irradiated in ECP was increased with Cl element detected. Surface free energy of all CFs was improved obviously after irradiation, and CFs irradiated in ECP had higher surface free energy compared with CFs irradiated in Ar. So they provided a different rule for the property change of different fibers after gamma-ray irradiation, which could provide insights for understanding the different conclusion in previous work, and offer a new possibility to the radical alteration of CF properties in further low-cost use of gamma rays.

3.4. CNT modification of carbon fiber and its effect of interphase modified with POSS and CNTs

Recently, nanomaterials have been widely used as reinforcements in the fibers reinforced polymer composite interphase in order to improve interfacial adhesion, toughness and heat resistance, etc, because of their unique size effect, high specific surface area and chemical activity. Carbon nanotubes, graphene oxide, polyhedral oligomericsilsesquioxanes (POSS), ZnO nanorods, SiO$_2$ nanoparticles etc. have been introduced into the interphase by using different strategies. In this section, progress of interphase modification with POSS and CNTs is summarized.

Recently, POSS has attracted much interests as a new modification technology in the field of composite materials [60]. Every POSS molecule possesses eight organic groups, which provides them with high reactivity and compatibility compared to other inorganic components, such as SiO$_2$ or CNTs. Moreover, these organic groups, which can further react based on the final application, make POSS a versatile nanoparticle. According to matrices, POSS with different organic groups are used as coupling agents between the inert fibers surface and polymer matrices to improve the overall properties of the resulting composites. They are introduced onto the carbon fiber surface through chemical reaction, gamma-ray radiation or simple solution dipping method [61]. Afterward, the polarity, wettability and roughness of carbon fiber surface can be effectively increased.

The interfacial adhesion is improved due to the chemical bonding formed among organic groups of POSS, fibers surface and matrices. Numerous POSS at interphase can also increase impact toughness of composites through inducing a great deal of cracks to absorb fracture energy [62]. In addition, the POSS modified carbon fiber composites also present improved heat, oxidation and chemical resistance. Due to the diversity of POSS, we can choose POSS with different organic groups to meet requirements according to different matrices, for example, POSS with unsaturated groups is used for unsaturated polyester and POSS with hydroxyl groups is used for silicone [62–64].

In recent, Guo et al. [62] grafted the amino-POSS on the carbon fibers surface which achieved by the reaction of the spiralphosphodicholor (SPDPC). After grafting with a combined SPDPC and amino-POSS, they found that the ILSS of the composites increased about 22.9%. The improvement of performance resulted from the well interfacial properties that caused by the improvement of surface roughness. In addition, our group [63] treated carbon fibers surface with using two different functional (mono-functional (methacrylolsobutyl) and multifunctional (methacryl)) POSS. After grafting with both kinds of POSS, we found the wettability and roughness of the carbon fibers that grafted with both kinds of POSS were almost the same, but they were higher than that of the untreated carbon fibers. However, the ILSS, IFSS and impact energy of the UPR composites reinforced with methacryl POSS grafted carbon fibers were much higher than those of the UPR composites reinforced with methacrylolsobutyl POSS grafted carbon fibers. From the FMAFM observations of the impact fracture surfaces, we discovered that the interfacial adhesion between the carbon fibers grafted with methacryl POSS and the resin was much better than that between the carbon fibers grafted with methacrylolsobutyl POSS and the resin (as shown Fig. 11). All of these results showed that the interfacial strength improvement for the methacryl POSS grafted carbon fibers/UPR composites was attributed to two factors: (1) the enhanced mechanical interlocking and (2) the chemical bonding on the interface. And the chemical bonding at the interface of carbon fibers/UPR composites played the most important role compared with other factors.

CNTs, due to its high mechanical properties and similar composition with carbon fibers, have been used to modify carbon fiber surface. Up to date, several methods have been developed, such as growing CNTs directly on carbon surface by CVD [66,67], coating fibers surface with CNT-containing sizing [68], chemical
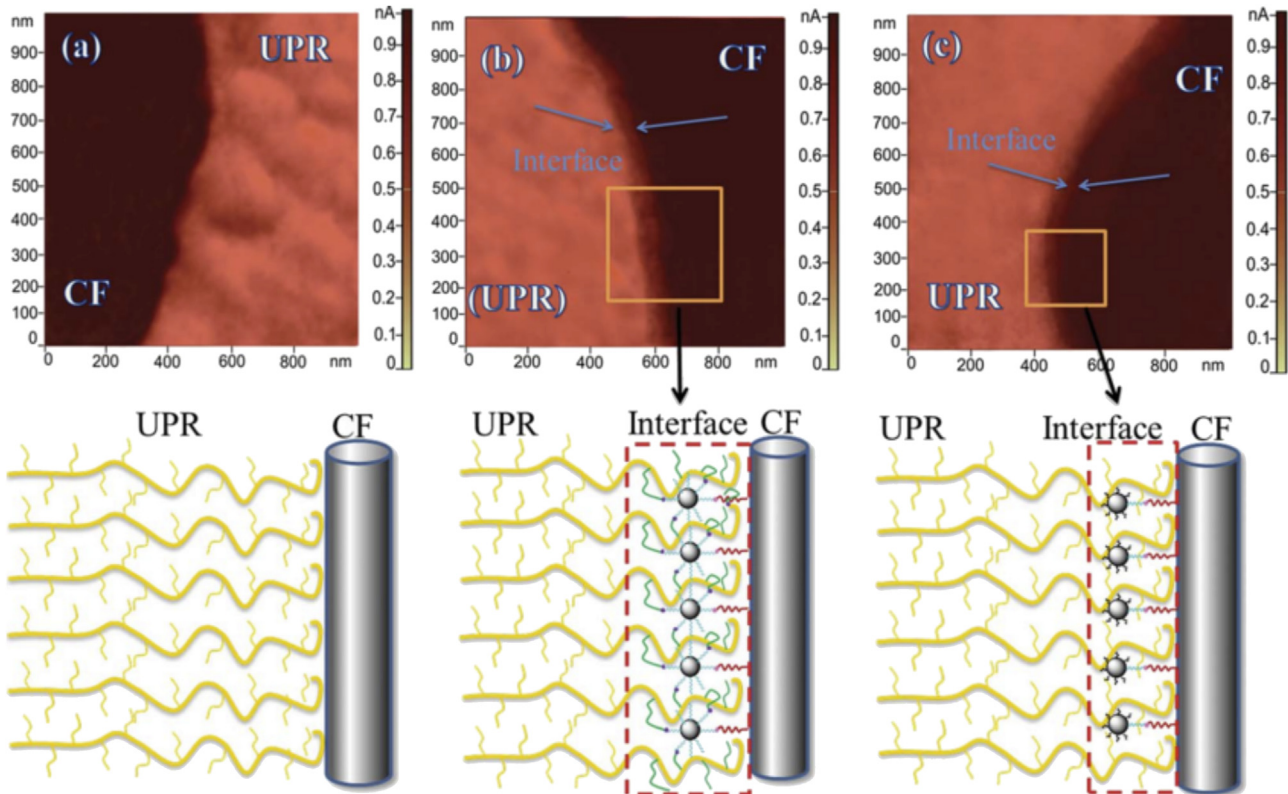
Fig. 11. (a–c) Force modulation AFM images and the sketch of as-received, methacryl POSS grafted and methacrylolsobutyl POSS grafted CFs for the CFs/UPR composites [62].

grafting of CNTs onto the functionalized fibers [69] and electrophoretic deposition [70,71]. There have been many references concerning these technologies in the last two decades.

Recently, Seo et al. [66] used the CVD method to graft CNTs directly on carbon fibers at low temperatures. The interface strengthen between carbon fibers and polymer matrix increased significantly and the mechanical properties of the fibers were not remarkably degraded. It meaned that grafting CNTs directly on carbon fibers using the CVD method is a good way to improve the performance of the carbon fibers. In addition, Lee [67] et al. found that CVD process itself did not cause any damages in the carbon fibers but instead healed them, if the proper CVD process time was maintained. And the catalyst coating and nanoparticle formation

were the main processes responsible for the reduced tensile strength in the carbon fibers. So they presented that proper CVD process condition was a key factor to effect the peformance of carbon fibers. Fig. 12 a shows schematic diagram of the CNTs directly grow on CF surfaces using CVD method, b–e figures show the morphologies of the CNTs grown on the carbon fibers according to the CVD method.

Moreover, Yu et al. [69] found that the tensile strength and the interfacial properties of carbon fiber can be concurrently improved by growing CNTs on their surface using CVD method, if the thickness of the catalyst coating and CVD conditions can be controlled properly. They discovered that grafting the CNTs on carbon fibers surfaces can repair some of the damage incurred during the
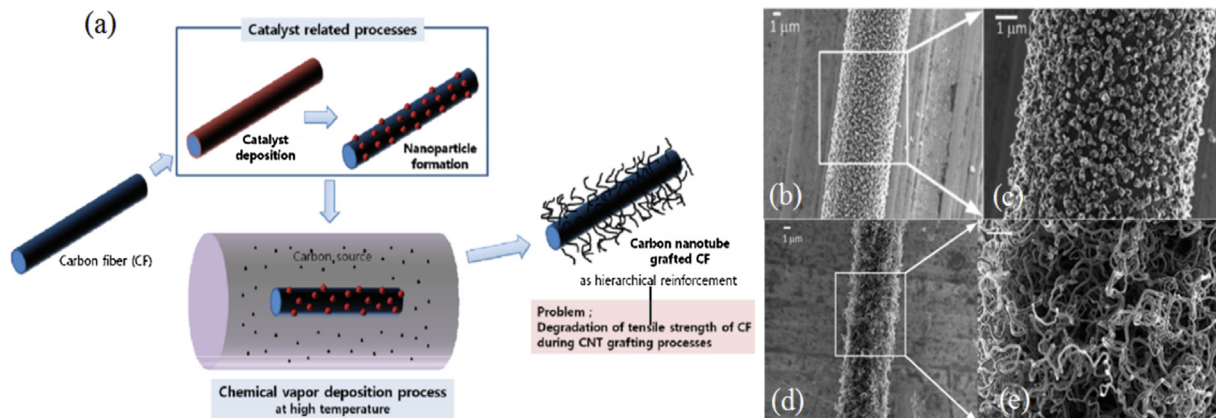

Fig. 12. Schematic diagram of the catalytic growth of CNTs on the CF surfaces. (b–e) show the morphologies of the CNTs grown on the carbon fibers according to the CVD method [68].

formation of catalyst nanoparticles, an increase in the carbon crystal size, and the formation of crosslinks of neighboring crystals by CNT by the CVD process (as shown in Fig. 13) which are the main reasons for the improvement, about 14%tensile strength increased. Expect for the CVD method, Brunner et al. [70] achieved to graft CNTs on carbon fibers surface continuously using the electrophoretic deposition method. This method can be operated under stable conditions for several hours and treated the carbon fiber surface on laboratory-scale. Meanwhile, the introduction of CNT on the carbon fiber can improve the interfacial adhesion property significantly.

Recently, a new strategy which introduces another nano-component with high reactivity on CNT surface or between fibers and CNTs has been developed. It not only uses the mechanical enhancement of CNTs to increase composite interlaminar strength, but also improve wettability and form strong chemical bonding at the interphase. For example, surface reactivity and wettability of carbon fiber and overall performance of composites can be obviously improved when amine-functionalized CNTs are grafted on octaglycidyldimethylsilyl POSS modified carbon fiber surface. Using this strategy, interphase with different complex nano-structure can be formed, which can optimize material performance according various requirements.

Besides the lastest method metioned above, recently, Feng et al. [71] proposed an efficient and robust route to functionalize CFs, based on dopamine chemistry, through a simple dip-coating procedure. They inverted CFs from amphiphobic to hydrophilic with deposition of polydopamine film. Furthermore, using polydopamine as a bridge, the hydrophilic functionalized CFs transformed to be oleophilic after following octadecylamine grafting. To illustrate applications of this functionalization strategy, they added 15 wt % functionalized CFs into polar epoxy and nonpolar poly(ethylene-co-octene), and as a consequence, their tensile strength respectively increase by 70 and 60%, which showed greater reinforcing effect than the unmodified ones (35 and 35%). It meaned the functionalized fibers produced excellent interfacial interaction with polymer matrices. Meantime, this simple approach was facile and robust enough to allow further specific functionalization to adjust surface properties. We believe these findings may lead to the development of new efficient strategies for surface functionalization of CFs that are of great interest to the industrial field.

3.5. Uniform modification of 3D woven

3D reinforced structures have been given focus on by more and more researchers [72–74]. The idea of 3D reinforced structures is derived from pile fabrics, needled felts, and stitched felts. These structures have better interlaminar performance than 2D cloth, but they are far from perfect. Their interlaminar shear strength, isotropic properties, and impact toughness must be modified to further improve. Many investigators have studied and developed 3D and multidirectionally reinforced materials. There are mainly four types of 3D fabrics, namely woven types (WT) [75], knit types (KT) [76], orthogonal nonwoven types (ONT) [77], and braid types (BT) [78]. Such developments are a consequence of the requirements of the national defense area, where multidirectional reinforcements are required and mechanical and thermal stresses are also involved.
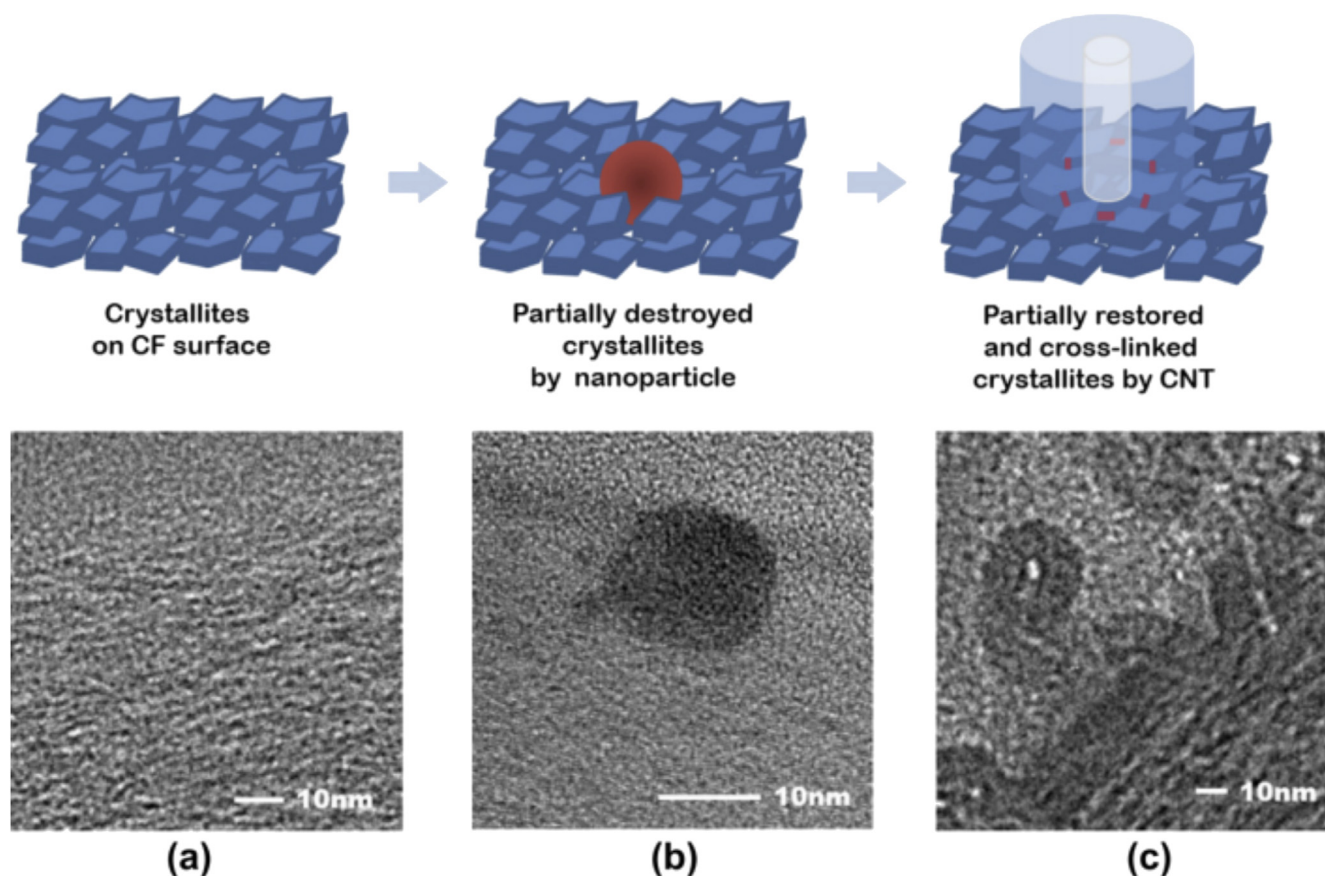

Fig. 13. A schematic diagram explaining the microstructural changes of a CF surface during the CNT growth process: (a)original CF surface, (b) nanoparticles formed and partly immersed inside the CF surface, incurring some damage, (c) the CNT-grafted-CF surface, showing an increased number of carbon crystals due to catalytic graphitization [69].

When 3D wove without previous surface modification was applied, the physical–chemical interaction between carbon fibers and its reinforced matrix is not strong enough, because of the inert surface property of carbon fiber surface, which will directly influence the interfacial performance of the composite system. A variety of surface treatments have been applied to carbon fiber to increase the interaction between the fibers and the resin matrix, including oxidation methods [79] (gas oxidation, chemical oxidation, electrolytic oxidation and plasma treatment, etc.) and non-oxidation methods [80,81] (coating method, coupling agent method and vapor deposition method). For 3D wove, the fibers surface modification is different from that for the filament. The desired treatment effects were not only for improving the interfacial adhesion between the fibers and the matrix but also for getting a uniform treatment throughout the fabrics. Thus, among those treatments, only some of treatments are suitable for surface modification of 3D wove, due to the thickness of 3D wove. The surface modification methods cannot penetrate into the inert of 3D wove and be used for the 3D wove surface modification. Based on the current attempts, impulse type anodic oxidation method for carbon woven has been chose to treat 3D wove, due to the easy penetration of gas and liquid, the gas oxidation, and the oxidation includes ozone oxidation [82], and electrolytic oxidation [83].

The gas oxidation can be achieved by heat treatment in air, oxygen (O_2) or ozone (O_3). Obviously, ozone has the most possibility for the surface treatment for 3D wove. However, the problem also is the thickness of the 3D wove. As we know, the excessive oxidation will also destroy the strength of carbon fiber. So it usually appears that it is excessive oxidation for outside of 3D wove when it is optimal oxidation for inside of 3D wove. Influence of thickness on distribution of gas concentration is shown in Fig. 12 a. To solve this problem, the pulse ozone oxidation has been employed. In every circle, the positive and negative pressure can force the ozone penetrate into the inside of 3D wove. Different effects of oxidation treatment on surface and internal fibers in 3D fabric are shown in Fig. 14b. With the pulse ozone oxidation, the homogenous oxidation for 3D wove has been achieved (as seen in Fig. 14c).

There is also the same problem for electrochemical treatment for homogeneous oxidation for 3D wove. Using traditional continuous electrochemical treatment method, concentration polarization will induce different treatment levels along the thickness direction of 3D fabric. Cao et al. [84] proposed a novel treatment method for 3D fabrics to obtain uniform treatment through impulse electrochemical treatment. In her treatment for 3D fabric, ammonium bicarbonate solution was used as the electrolyte with the concentration of 5.0wt%. Fresh electrolyte solution was used for each condition. The specific current density for the treatment was about 120 mA/g. It was precisely controlled by a constant current and voltage source. The total treatment time (total working time)
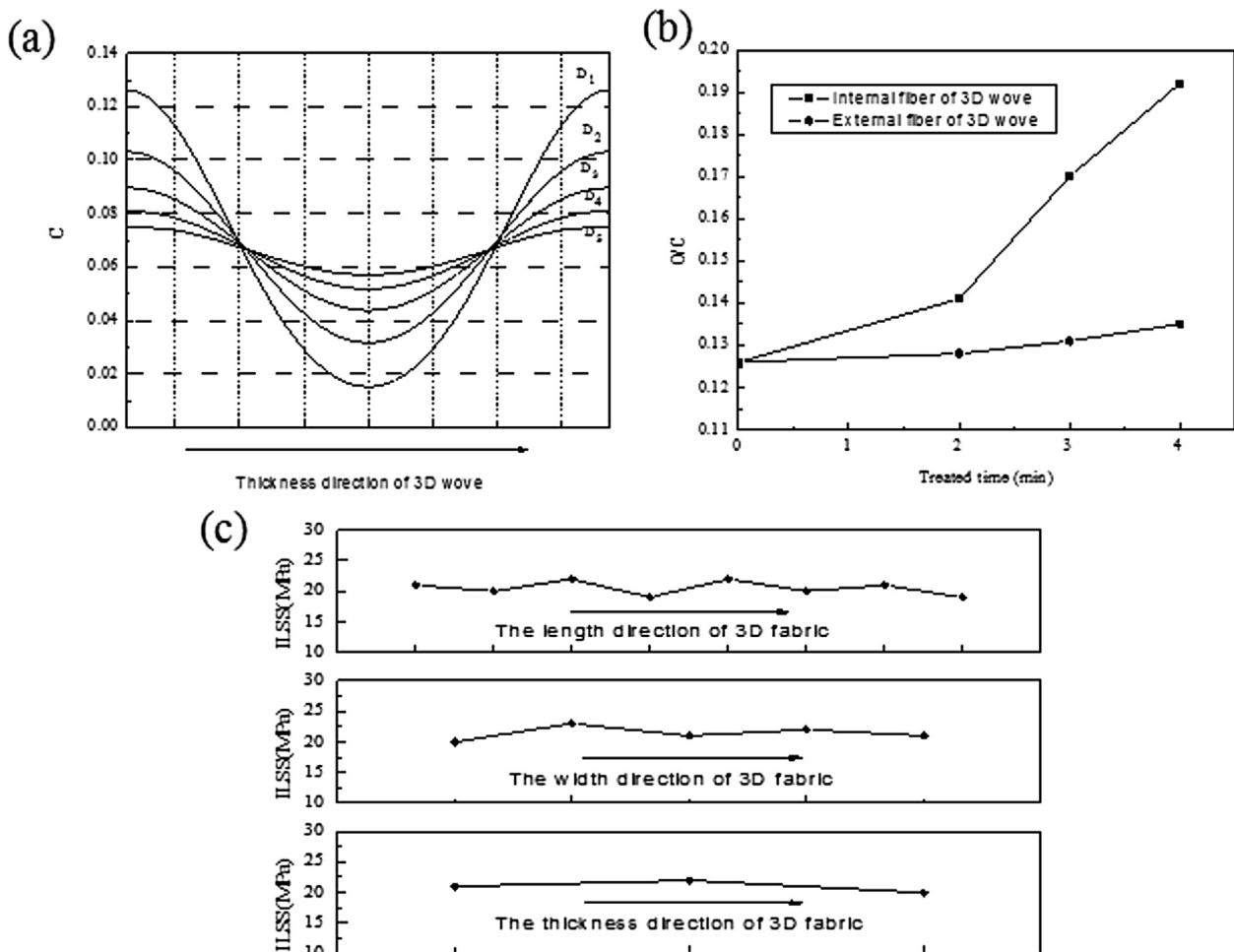

Fig. 14. (a) Influence of thickness on distribution of gas concentration. (b) Different effect of oxidation treatment on surface and internal fibers in 3D fabric. (c)Change curves of the average ILSS values in 3D fabric reinforced composite.

was about 4 min, and the interval time (off period time) was 5 min. The intermittent times were varied from 1 to 9 which divided the treatment time averagely. After treatment, the IFSS of the surface region and the interior region along the thickness direction of the fabric composites were all obtained, as shown in Fig. 13b. After treatment, IFSS of fibers of different regions increased. Furthermore, the IFSS value between the different regions was near equal. When the intermittent time achieved 7, the IFSS values at both regions all reached the maximum values and the gap between them was minimal. As the intermittent time reached 9, the IFSS at both regions were all decreased slightly. Thus, the interior region of the fabric could be activated by the treatment. The degrees of the treatment were different for the fibers in different regions of the fabric. And proper intermittent treatment almost achieve the optimum effect through the fabric.

4. Development tendency

This review provides a comprehensive review of the interfacial characterization methods of carbon fiber composites, including AFM to characterize thickness and modulus of interphase, XPS to characterize the distribution of surface coating and the diffusion between resin and sizing of fibers, XRD to characterize interfacial residual stress and SAM to characterize molecular assembly of carbon fiber, etc. With the development of characterization methods, we consider that fiber surface or composite interfaces have been well characterized. The development trend of characterization methods still is inventions for in-situ characterization methods. Due to the complex of composite interface, the method to characterize in-situ that was relevant to interface formation processes has so far been elusive. Meanwhile, we also reported some novel methods of modifying the carbon fibers, including Gamma-ray irradiation modified carbon fiber and uniform modification of 3D woven to carbon fiber. The interfacial adhesion of carbon fiber and resin composites was significantly increased by these methods. More importantly, great deals of these methods have been industrial applications.

At present, many researchers are committed to the surface modification of the carbon fiber reinforced composite material. And nano-system modification of the carbon fiber reinforced composite material has become one of the schemes for the pursuit of higher performance materials, such as grafting CNTs onto carbon fibers, dopamine modification et al. The comprehensive performance of composite material can be enhanced at different levels by introducing nano-component to fibers reinforced composites system in different ways (including to form specific nanostructure on fibers interface or to introduce nanophase to polymer matrix). Comparing to those traditional modified methods, most studies are theoretical, so industrialization efficiently modification methods have always been a hotspot studied in materials science field. Because of easy operation and obvious effect, anodic oxidation method and ultrasonic forced impregnation method are the main modification methods used in industrial field currently.

Thus, further sustained research effort is still required before an appropriate method for carbon fiber surface modification can be discovered. The interfacial design and control is still a promising direction to treat the carbon fiber surfaces.

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