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Influence of fibre surface oxidation–reduction followed by silsesquioxane coating treatment on interfacial mechanical properties of carbon fibre/polyarylacetylene composites

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Abstract

Carbon fibre was treated with oxidation–reduction followed by silsesquioxane coating method to improve the interfacial properties of carbon fibre/polyarylacetylene (CF/PAA) composites. The treatment method was divided into three phases, i.e., oxidation with oxygen plasma, reduction with $LiAlH_4$, and coating treatment with vinyl silsesquioxane (VMS–SSO). The fibre surface composition and functional group were analyzed using X-ray photoelectron spectroscopy (XPS). The polar functional groups, especially C–OH which could react with Si–OH on silsesquioxanes, were increased after redox reaction. VMS–SSO coating treatment imported vinyl groups which could react with PAA resin during PAA cure process. The surface morphology of carbon fibre was observed by atomic force microscopy (AFM) and scanning electron microscopy (SEM). The mechanical interfacial properties of the CF/PAA composites were characterized by short-beam bending testing method. Interlaminar shear strength (ILSS) of the CF/PAA composites in different treatment phases were increased by 31.7%, 28.8%, and 59.3%, respectively. The conclusion that oxidation–reduction followed by silsesquioxane coating treatment is an effective method to improve the interfacial properties of the CF/PAA composites can be drawn. This method can be used in other resin systems if the functional groups on silsesquioxane are changed according to those in resins.
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Keywords: A. Carbon fibre; A. Polymer-matrix composites; B. Interface; E. Surface treatments; Coating

1. Introduction

Polyarylacetylene (PAA) is going through increasing development in the field of advanced heat resistant composites owing to its outstanding heat resistance and excellent ablative properties [1–7]. The advantages of PAA resin over the state-of-the-art heat resistant resin, for example phenolic resin, have been reviewed by Huang [8]. The main potential applications of PAA resin are used in conventional resin matrix composites with ultralow moisture outgassing characteristics and improved dimensional stability suitable for spacecraft structures, as an ablative insulator for solid rocket motors, and as a precursor for carbon–carbon composites. Carbon fibre reinforced PAA composites (CF/PAA) undoubtedly play a very important role in all these fields [5,7,8]. Unfortunately, the mechanical properties of the CF/PAA material are not yet sufficiently satisfactory to replace the heat resistant composites used widely currently such as carbon or graphite reinforced phenolic resin. The mechanical properties of carbon fibre reinforced resin matrix composites depend on the properties of CF and matrix, especially on the effectiveness of the interfacial adhesion between CF and matrix [9–13]. PAA has high content of benzene ring and hence a highly cross-linked network structure, which render the material brittle [3,8]. Moreover, the chemical inert characteristics of the CF surface lead to weak interfacial adhesion between fibres and non-polar PAA resin [8,14].

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To ensure that the material could be used safely in complicated environmental conditions and to exploit the excellent heat resistant and ablative properties more effectively, it is necessary to improve the mechanical properties of the CF/PAA composites. To achieve this purpose, two kinds of methods can be used. One kind of method is to improve the properties of PAA resin by structural modification [15] or by intermixing other resins, such as phenolic resin [14], with PAA. The other is treatment of CF surface. The treatment of carbon fibre surface has been studied for a long time and several methods such as heat treatment [16], wet chemical or electrochemical oxidation [9,17,18], plasma treatment [10,12,19], gas-phase oxidation [20], and high-energy radiation technique [13] have been demonstrated to be effective in the modification of the mechanical interfacial properties of composites based on polar resins such as epoxy. Huang has studied the influence of fibre surface ozone oxidation treatment on the interfacial mechanical properties of the CF/PAA composites [8].

As an important hybrid material, silsesquioxane (SSO) has been studied for some years. The name of SSO derives from the non-integer (one and one-half or sesqui) ratio between oxygen and silicon atoms [21]. It relates to a class of compound that contains a silicon–oxygen nanostructural skeleton with intermittent siloxane chains (general formula $RSiO_{1.5}$), R can be H, alkyl, alkylene, aryl, aromatic alkylene or their derivative groups [22], which are reactive or inert functional groups. SSO can exist in several structural types such as random, ladder, cage, and semi-cage structures. It can be prepared by the hydrolytic condensation of an organic siloxane ($RSi(OR')_3$), where R and R′ are different organic groups [23]. SSO with a cage structure is also called polyhedral oligomeric silsesquioxane (POSS, or $(RSiO_{1.5})_n$, where $n = 6, 8, 10, \ldots$). POSS has been used as a new chemical feedstock technology for the preparation of organic–inorganic hybrid materials [24]. Literature concerning incorporating dispersed SSO into traditional organic polymer systems has been published and the amount of them increases year by year. New hybrid inorganic–organic polymer systems have been produced with remarkable enhancements in mechanical and physical properties, including dramatic increases in both glass transition and decomposition temperatures [25,26], reduced flammability [27], increased moduli [28,29], and oxidation resistance [30,31].

In the present work, carbon fibres were oxidized with oxygen plasma and then were deoxidized with $LiAlH_4$ followed SSO coating treatments. The effects of the treatment on the fibre surface and the mechanical interfacial properties of the CF/PAA composites were studied. The fibre surface composition and functional group were examined by using X-ray photoelectron spectroscopy (XPS). The surface morphology of the fibre was observed by atomic force microscopy (AFM) and scanning electron microscopy (SEM). The interfacial mechanical properties of the CF/PAA composites were characterized by short-beam bending test method.

2. Experimental

2.1. Materials

PAA resin, a brown liquid with the density of ~1.05 g cm^{-3} and the viscosity of 200–3000 mPa s (corresponding to a temperature changing from 90 to 30 °C), was supplied by the Aerospace Research Institute of Material and Processing Technology (Beijing, China). PAA resin is the mixture of *m*-diethynylbenzene, *p*-diethynylbenzene, and phenylacetylene. Poly(acrylonitrile) (PAN) carbon fibres (3×10^3 single filaments per tow, tensile strength was 3.38 GPa, average diameter was 7 μm, density was 1.76 g cm^{-3}, linear mass was 0.161 g m^{-1}) were obtained from Jilin Carbon Co. (Jilin, China). Silsesquioxane, named VMS–SSO (the mixture of different structures was shown in Fig. 1), was synthesized by the hydrolytic condensation method. Vinyltrimethoxysilanes (VMS), which was the coating precursor subjected to hydrolytic condensation, was acquired from Shuguang Silane Coupling Factory (Nanjing, China) and used as received. Most of chemicals used in this study, including analytically grade ethanol (C_2H_5OH), formic acid (HCOOH), acetone, and tetrahydrofuran (THF) were purchased from the First Factory of Chemical Agents (Tianjin, China). $LiAlH_4$ was purchased from Dow Corning and used as received.

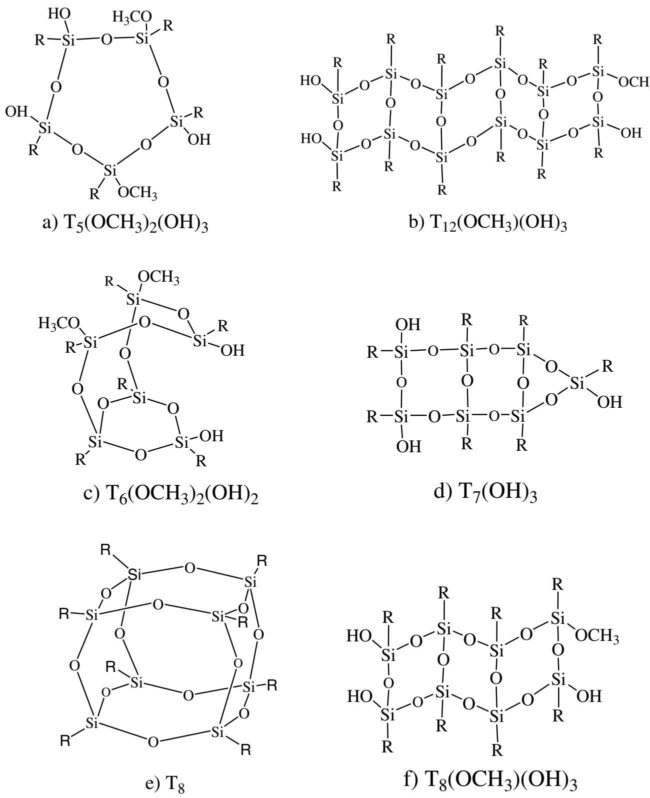
a) $T_5(OCH_3)_2(OH)_3$
b) $T_{12}(OCH_3)(OH)_3$
c) $T_6(OCH_3)_2(OH)_2$
d) $T_7(OH)_3$
e) T_8
f) $T_8(OCH_3)(OH)_3$

Fig. 1. Some typical structures of VMS–SSO (R is $-CH{=}CH_2$).

2.2. Methods

The carbon fibre surface treatment process was shown in Fig. 2. One of the experiments was described as follows. The oxygen plasma treatment was carried out in a plasma processor, Corona 2000 (Nanjing, China) generator where cold oxygen at a pressure of 1.00 ± 0.01 mbar was excited by using microwave energy. Several bundles of carbon fibre were wound up on a glass frame and placed into a reactor. The microwave power and the exposure time to the plasma were 60 W and 5 min, respectively. The oxygen was continued inputting for 1 h to oxidize completely and form functional groups including oxygen after the plasma oxidation treatment. The $LiAlH_4$/THF saturated solution was used to reduce CF surface functional groups for 1 h at 65 °C. HCl and distilled water were used to wash CF in sequence till the washed water was neutral and then fibres were dried. 2 wt.% VMS–SSO/THF solution was used to coat CF surface. In other experiments, the exposure time to plasma is different (0 min, 2.5 min, 7.5 min and 10 min).

Both untreated and treated carbon fibres were cleaned with THF in an extractor for 48 h before testing the fibre surface properties in order to remove the unreacted VMS–SSO from the fibre surface.

X-ray photoelectron spectroscopy (XPS) measurements were performed using a VG Scientific Escalab MK II spectrometer (VG Co.) equipped with a monochromatic Mg Kα X-ray source (1253.6 eV). Carbon fibres were placed in a specially designed support ensuring that no signal was observed from the sample holder. The pass energy was set at 150 and 50 eV for the survey and the high resolution spectra, respectively. The instrument was operated with an analyzer chamber pressure of 2.6×10^{-7} Pa. The step size was 1.00 eV for the survey spectrum and 0.060 eV for the high resolution spectra. All spectra were energy calibrated by assigning 284.5 eV to the C1s binding energy of the graphitic peak. Surface atomic composition were calculated from the areas of the peaks from survey spectra after fitting of a Shirley background, which was subtracted prior to quantification and correcting the relative peak areas using the manufacture's sensitivity factors. High resolution envelops were fitted using mixed Lorentzian–Gaussian curves.

The effects of the treatment on the fibre surface morphology were observed by using atomic force microscopy (AFM) and scanning electron microscopy (SEM). Individual fibre was examined in Solver P47 AFM/STM system (NT-MDT Co., Russian) and S4700 SEM (HITACHI, Japan), respectively. During the process of AFM test, all images were obtained in semi-contact mode (tapping mode), which was more suitable for scanning the arched surface of a carbon fibre than the contact mode. During the process of SEM testing, the samples were metallized with a thin layer of platinum, 10 nm in thickness, due to the poor conductivity of the VMS–SSO coating on the carbon fibres.

The unidirectional long carbon fibre reinforced PAA composites were made using both untreated and treated carbon fibres. Curing was performed in a compression moulding machine, and the content of the resin content of the composites was controlled at about 35 wt.%. The curing process was involved heating at 120 °C for 2 h, 140 °C for 2 h, 180 °C for 2 h, 200 °C for 2 h, and 250 °C for 0.5 h. During the curing process, the pressure was 2 MPa which was loaded after the temperature being increased to 120 °C. When the curing process had finished, the mould was cooled to room temperature with the pressure being maintained. All composite samples were about 6 mm in width and 2 mm in thickness.

The interlaminar shear strength (ILSS) of the CF/PAA composites were measured on a universal testing machine (WD-1,Changchun, China) using a three point short beam bending test method according to ASTM D2344. Specimen dimensions were 20 mm × 6 mm × 2 mm, with a span to thickness ratio of 5. The specimens were conditioned and an enclosed space where the test was conducted was maintained at room temperature. The specimens were measured at a rate of cross-head movement of 2 mm min^{-1}. The ILSS, Γ, for the short-beam test was calculated according to the following Eq. (1):

$$\Gamma = \frac{3P_\text{b}}{4bh}, \tag{1}$$

where P_b is the maximum compression force at fracture in Newtons, b is the breadth of the specimen in mm, and h is the thickness of the specimen in mm. Each ILSS value

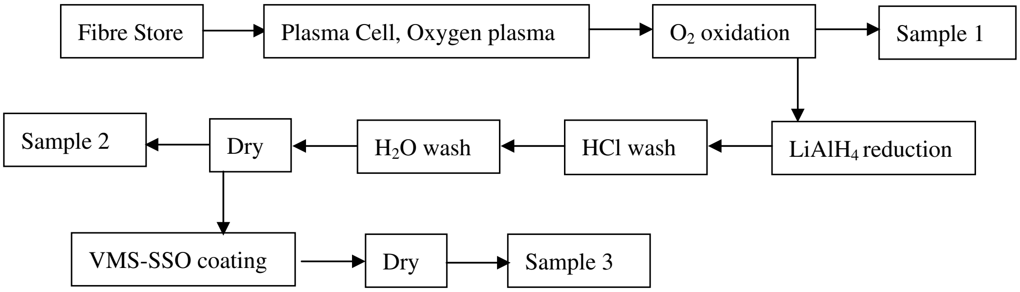

Fig. 2. Schematic diagrams of carbon fibre treatment process (sample 1 is oxygen plasma oxidation, sample 2 is $LiAlH_4$ reduction, sample 3 is VMS–SSO coating).

reported was the average of more than eight successful measurements.

3. Results and discussion

3.1. ILSS of CF/PAA composites

The CF treatment process could be divided into three phases, i.e., oxygen plasma oxidation, $LiAlH_4$ reduction, and VMS–SSO coating treatment. The time of every treatment phase could affect the CF surface treating effect which resulted in the difference of the adhesion between CF and PAA resin. The $LiAlH_4$ reduction time was decided according to the experimental parameter of Lin [32]. The VMS–SSO coating concentrations and treatment time were decided according to Huang [33] who had optimized VMS–SSO coating treatment parameters. Thus the oxygen plasma oxidation time became the emphasis of the present investigation. The effect of oxygen plasma oxidation time on the ILSS of the CF/PAA composites was shown in Fig. 3. The microwave power (60 W), the $LiAlH_4$ reduction and VMS–SSO coating treatment time were kept in the same level in order to study the influence of oxidation time on the ILSS. The adhesion between CF and PAA resin was weak and the ILSS of untreated CF/PAA composite was only 30.2 MPa. The ILSS of the CF/PAA composite was 29.2 MPa after reduction and there was a negligible change in the ILSS of the composites. The $LiAlH_4$ reduction phase had small effect on the ILSS. The ILSS could be increased to 34.2 MPa which resulted from the introduction of VMS–SSO coating. The load could be transferred effectively from the resin to the fibre through the VMS–SSO layer around the fibre. Siloxane coatings were effective to increase the ILSS of carbon fibre reinforced resin matrix composites [34]. The ILSS was increased when the oxygen plasma oxidation time was prolonged. The value of the ILSS could reach the maximum when the oxygen plasma oxidation time was 7.5 min and then the ILSS began to decrease. The maximum of the ILSS was 39.8 MPa, 38.9 MPa, and 48.1 MPa, respectively, in different treatment phase. Compared with the untreated one (30.2 MPa), the ILSS of the CF/PAA composites at optimal treatment time were enhanced by 31.7%, 28.8%, and 59.3%, respectively. The ILSS of the CF/PAA composites were increased largely, which resulted from two factors, one was the oxygen plasma treatment and the other was the VMS–SSO coating treatment, after complete treatment. Although the reduction phase was also important during all the treatment process, there were a few influence of reduction on the ILSS of the composites according to the present results. SEM, AFM and XPS were used to characterize the surface of the untreated and treated CF in order to explain the change of the ILSS.

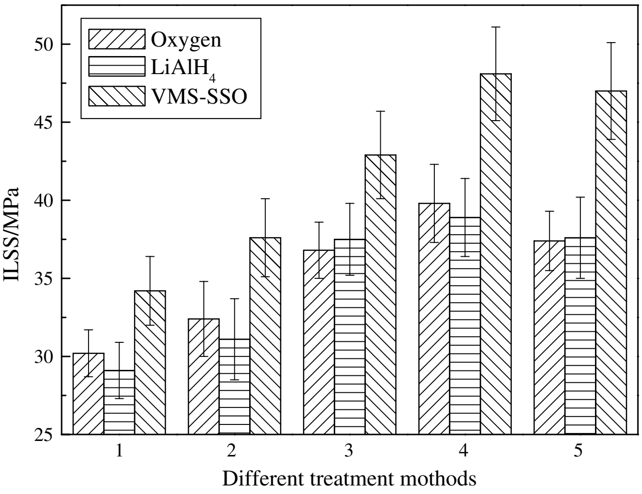

Fig. 3. Effects of CF surface treatment on ILSS of CF/PAA composites (the treatment sequence was oxygen plasma oxidation, $LiAlH_4$ reduction and then VMS–SSO coating treatment. The oxygen plasma treatment times were different from No. 1 to No. 5 but the $LiAlH_4$/THF solution treatment time and the VMS–SSO/THF solution treatment time were same in every kind of sample. The oxygen plasma treatment times were 0 min, 2.5 min, 5 min, 7.5 min and 10 min, respectively, from No. 1 to No. 5. The power was 60 W. $LiAlH_4$/THF saturated solution reduction time was 1 h. VMS–SSO/THF coating solution treatment time was 0.5 h).

3.2. Surface topography analysis

Fig. 4 showed the SEM images of untreated, oxygen plasma oxidation, $LiAlH_4$ reduction, and VMS–SSO coating treatment carbon fibre surface, respectively. All samples were washed using THF in an extractor before the SEM tests. The surface of the untreated, oxygen plasma oxidation, $LiAlH_4$ reduction CF was clean while there were particles on the surface of VMS–SSO coating treating one. The surface of untreated CF was smooth and few shallow grooves that were parallel distributed along with the longitudinal direction of the carbon fibre appeared (as shown in Fig. 4(a)). There were many small deep grooves on the surface of carbon fibre after the plasma treatment (as shown in Fig. 4(b)–(d)) due to the etching of oxygen plasma. The $LiAlH_4$ reduction had no visible effect on the surface of CF. The particles on the surface of completely treated CF (Fig. 4(d)) suggested that there were chemical bonds between CF and VMS–SSO because VMS–SSO should be removed using THF if there was only physical action. The AFM three-dimensional topographies of CF were shown in Fig. 5. Five specimens were tested in order to study the surface morphology. The quantity of the carbon fibre surface roughness was calculated from the plane topography images, which was not presented here, by using the AFM software. Comparison of the three-dimensional AFM topography images of the carbon fibres, the difference in morphology showed that plasma etching could change the surface topography on a microscopic scale. Fig. 5(a) showed that the surface of the untreated carbon fibre was smooth, which was the same as that of SEM morphology. The mean value of peak height (MVPH) and the surface roughness (SR) were 66.8 nm and 28.5 nm, respectively. From Fig. 5(b), we could find that the surface topography was changed dramatically after the oxygen plasma

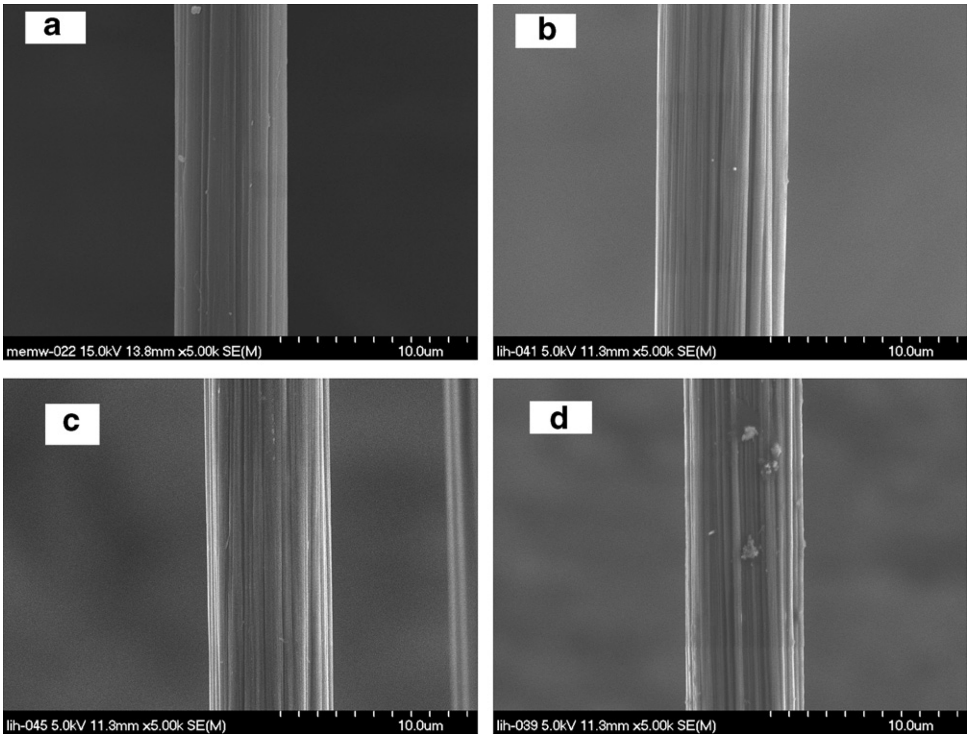

Fig. 4. SEM topographies of CF in different treatment phases, all samples were washed with THF before observation (a) untreated (b) oxygen plasma oxidation (c) $LiAlH_4$ reduction (d) VMS–SSO coating.

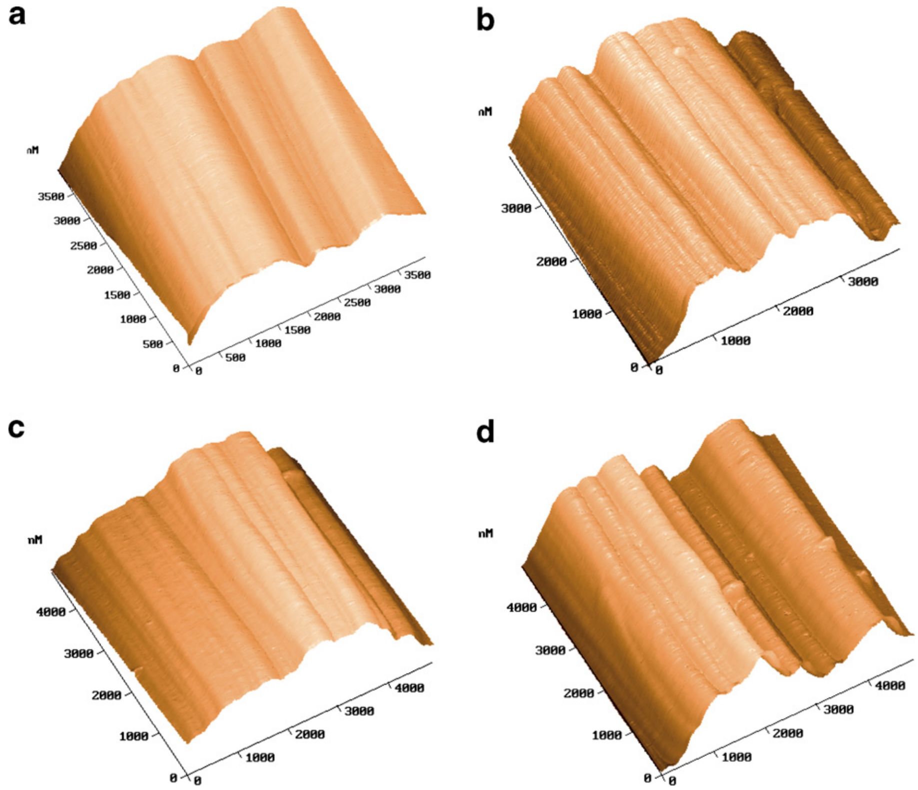

Fig. 5. AFM topographies of CF in different treatment phase, all samples were washed with THF before observation (a) untreated (b) oxygen plasma oxidation (c) $LiAlH_4$ reduction (d) VMS–SSO coating.

etching. The quantity of grooves was increased significantly which was proved by the variation of MVPH (135.6 nm) and SR (56.1 nm). Fig. 5(c) suggested that there was no obvious difference on the surface topography between oxidation and reduction, which was also proved with the variation of MVPH (133.5 nm) and SR (54.4 nm). The obvious change on the completely treated carbon fibre (Fig. 5(d)) was the appearance of the bulges and projections which resulted from the VMS–SSO coating. Both SEM and AFM topographies (Figs. 4 and 5(d)) proved that there were chemical bonds between carbon fibre and VMS–SSO coating. The functional groups (double bonds) in VMS–SSO coating could take part in the reaction of PAA resin during cure process, which was proved in other paper. Thus, there was a bridge made from VMS–SSO between carbon fibre and PAA resin in composites, which could also be proved with XPS analysis.

Table 1
XPS surface element analysis data of untreated and treated carbon fibre

Carbon fibre	C (%)	O (%)	Si (%)	O/C
Untreated	90.80	9.20	–	0.10
Oxygen plasma oxidation	86.30	13.70	–	0.16
$LiAlH_4$ reduction	90.34	9.66	–	0.11
VMS–SSO coating	83.27	15.56	1.17	0.19

3.3. XPS analysis

It is well known that XPS is a useful technique in the determination of chemical composition and functional groups of the fibre surface [35]. Survey spectra in the binding energy range from 0 eV to 1200 eV were obtained to identify the surface elements and carry out a quantitative analysis. The surface composition of untreated, oxygen plasma oxidation, $LiAlH_4$ reduction, and VMS–SSO coating treated carbon fibre was determined by XPS and the results were shown in Table 1. The XPS survey spectra showed distinct carbon and oxygen peaks, representing the major constituents of the carbon fibres investigated. A small amount of nitrogen was also observed from the spectroscopy, but it could be neglected because of its extremely low content. Silicon was detected from survey spectra of the completely treated carbon fibre surface although the samples were washed with THF. It was found that the surface C element concentrations of the untreated, oxygen plasma oxidation, $LiAlH_4$ reduction, and VMS–SSO coating treated carbon fibre samples were 90.80, 86.30, 90.34, and 83.27 at.%, respectively. The surface C concentration

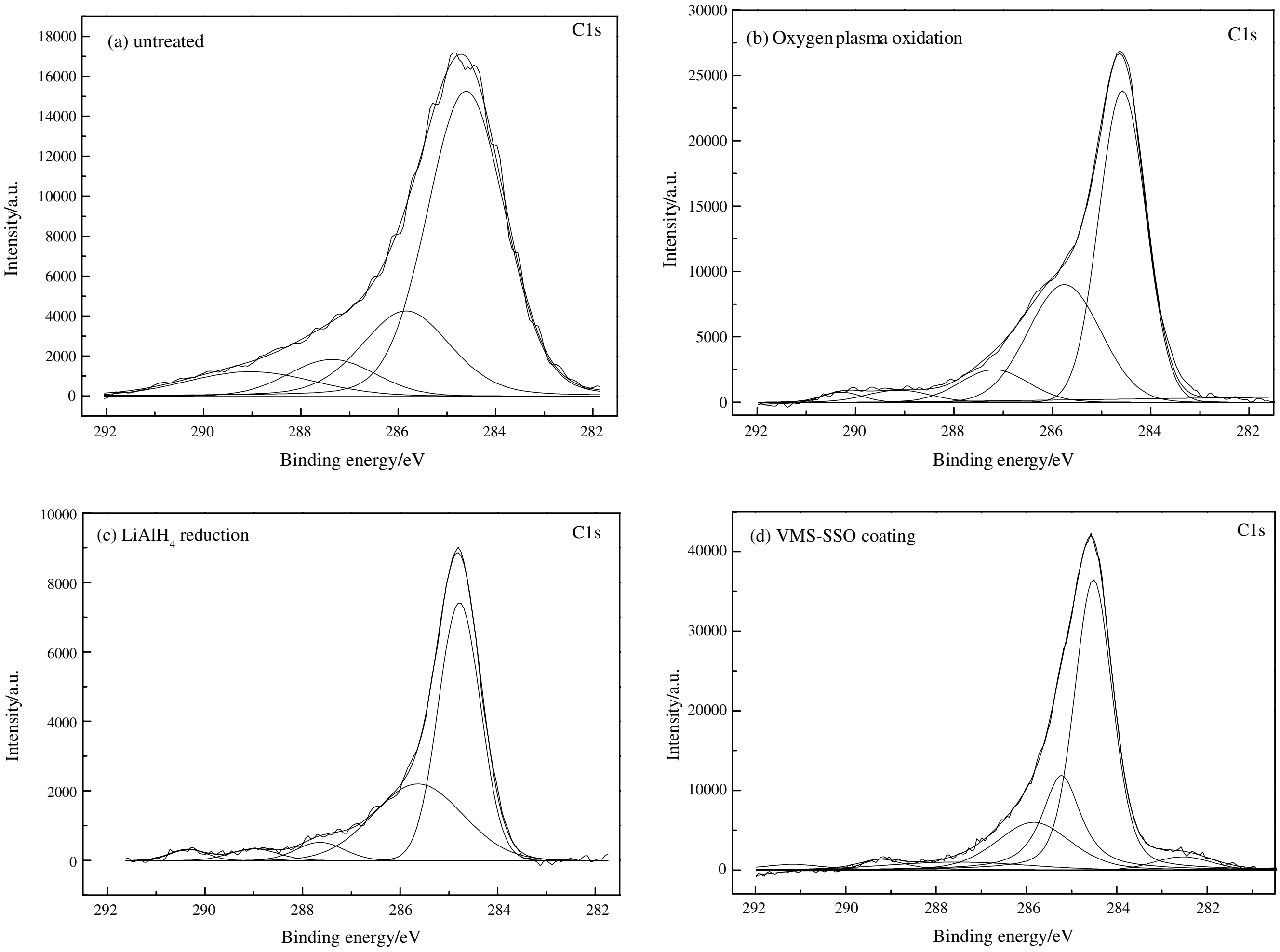

Fig. 6. C1s XPS spectra of untreated and treated carbon fibres.

in oxygen plasma oxidation and VMS–SSO coating treated carbon fibres were lower than that in the untreated one. While the surface C concentration in $LiAlH_4$ reduction treated carbon fibre was similar with that of untreated one. The O/C value of oxygen plasma oxidation treated carbon fibre was higher than that of untreated one. The O/C value of $LiAlH_4$ reduction treated carbon fibre had no remarkable change compared with that of untreated one. The O/C value of completely treated carbon fibre was the highest among all the samples because of the imported VMS–SSO. The change of O element on surface in oxidation–reduction process was helpful to graft VMS–SSO on CF surface. To make sure the modification mechanism, high resolution spectra of C1s was analyzed.

Fig. 6 showed the C1s peak fitted curves of XPS spectra of the fibre samples. The values of the binding energy (BE) and percent contribution (PC) of each curve fit peak were listed in Table 2. It was found that the C1s peaks could

Table 2
Contents of functional groups on carbon fibres before and after treatment

Carbon fibre		C1s photopeak						
		C=C	C–C	C–Si	–C–OH, –C–OR, –C=N	–C=O	–COOH, –COOR	Plasmon
Untreated	BE	–	284.62	–	285.92	287.34	289.10	
	PC	–	64.1	–	18.2	6.9	10.8	
Plasma oxidation	BE	–	284.56	–	285.78	287.18	289.12	290.29
	PC	–	55.2	–	32.1	8.3	2.8	1.5
$LiAlH_4$ reduction	BE	–	284.79	–	285.64	287.64	289.00	290.35
	PC	–	55.7	–	35.0	4.3	2.8	2.1
VMS–SSO coating	BE	282.56	284.54	285.24	285.86	287.55	289.25	291.29
	PC	3.2	51.9	20.0	16.0	4.7	2.7	1.5

BE (eV), PC (%).

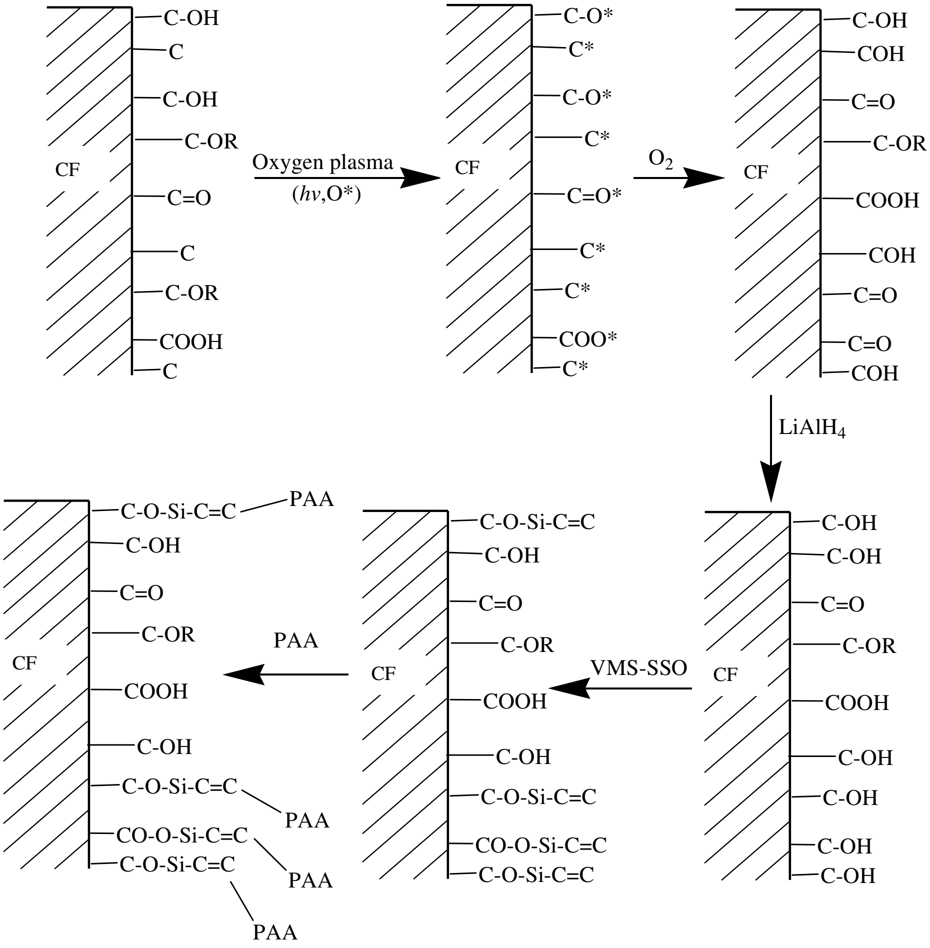

Fig. 7. Schematic process of CF treatment and CF/PAA composite structure.

be fitted to seven peaks, i.e., C=C, C–C, C–Si, –C–OH (–C–OR or –C=N), –C=O, –COOH or –COOR, and plasmon, respectively, after carbon fibres were treated with all process (Fig. 6(d)). The areas of –C–OH peak and –C=O peak in oxygen plasma oxidation carbon fibre (Fig. 6(b)) were larger than those of untreated carbon fibre (Fig. 6(a)) because of the oxidation of C–C, –C–OH at the action of oxygen plasma and oxygen. The content of –COOH or –COOR decreased due to the decomposability of them with the attack of oxygen plasma and then produce partly –C–OH or –C=O at the action of O_2. The content of –C–OH on $LiAlH_4$ reduction carbon fibre continued to increase and that of –C=O decreased at the same time because –C=O group was reduced to –C–OH with the action of $LiAlH_4$ (Fig. 6(c)). The content of –COOH or –COOR was kept stable before and after reduction because of the weak reducibility of $LiAlH_4$. There were C–Si and C=C on the surface of completely treated carbon fibre (Fig. 6(d)), which was consistent with the SEM and AFM characterization results. The changes of carbon fibre surface functional groups during all treatment process were schematically shown in Fig. 7. There was a chemical bond, which owed to the VMS–SSO, between treated carbon fibres and PAA resin. So the adhesion between carbon fibre and PAA resin was improved and the ILSS of the composites was increased after treated with this treatment method. The idea of the method can also be used in other resin systems because the functional groups of SSO are easily changed, for example SSOs with epoxy groups can be used in epoxy resin.

4. Conclusions

Carbon fibres were treated with oxidation–reduction followed by VMS–SSO coating method to improve the interfacial mechanical properties of the CF/PAA composites. Polar functional groups, including carboxyl and hydroxyl, on carbon fibre surface were imported after the oxygen plasma oxidation treatment. The quantity of carboxyl on carbon fibre surface was decreased and that of hydroxyl on carbon fibre surface was increased after the $LiAlH_4$ reduction treatment. The VMS–SSO coating was grafted onto the carbon fibre surface by the reaction of the hydroxyl in VMS–SSO and that on CF surface. The ILSS of the CF/PAA composites was increased by 59.3% at the end of treatment. The conclusion that CF surface oxidation–reduction followed by silsesquioxane coating treatment is an effective method to improve the interfacial mechanical properties of CF/PAA composites can be drawn. This kind of method could be widely used in different resin matrix composites by changing the functional groups on silsesquioxanes according to that on the resin matrix.

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