

Effects of silsesquioxane coating structure on mechanical interfacial properties of carbon fibre/polyarylacetylene composites

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Abstract Carbon fibres (CF) were treated with different coatings, including [3-(methacryloxy)propyl] trimethoxysilane (MPMS), [3-(methacryloxy)propyl] silsesquioxane (MPMS-SSO), and (methacryloxy)propyl polyhedral oligomeric silsesquioxane (Methacryl-POSS), to improve the interfacial properties of carbon fibre reinforced polyarylacetylene (PAA) matrix composites. MPMS-SSO was obtained from the hydrolytic condensation of MPMS. The complicated structure, including cage and ladder one, of MPMS-SSO may be assigned by Fourier transforms infrared (FT-IR) spectra, ^1H , ^{13}C and ^{29}Si nuclear magnetic resonance (NMR) and ultraviolet matrix-assisted laser desorption ionization time-of-flight mass spectrometry (UV-MALDI-TOF MS). Interlaminar shear strength (ILSS) was tested to investigate the effect of coating structure on the interfacial bonding. The values of ILSS of untreated and treated CF/PAA composites with different coatings (MPMS, MPMS-SSO and Methacryl-POSS) show that the treatment effect of Methacryl-POSS coating is the best one and the MPMS-SSO coating is better than that of MPMS coating. SEM micrographs of shear fracture of CF/PAA composites also suggested the different coating treatment effects. The differences of increasing degrees of ILSS indicate that the structure of coating is important when silsesquioxanes are used as coatings to treat fibre

surface for building up the adhesion and improving interfacial properties of fibre reinforced polymer matrix composites.

Introduction

The incorporation of strong and stiff fibres in a low-strength, low-modulus matrix results in considerable improvements in strength, stiffness and resistances to fracture. The interaction and adhesion between fibres and matrix has a significant effect in determining the properties of fibre reinforced resin matrix composite. The interface is defined as a region, which is formed because of bonding and interaction between the fibre and the matrix. The morphological features, chemical compositions, and thermo-mechanical properties of the interface, are distinct from bulk materials. The optimization of the fibre–matrix interfacial properties for improving the mechanical performance of composites is one of the most challenging tasks in designing new composite systems. Due to their outstanding mechanical properties, carbon fibres are very attractive materials to be employed as reinforcement in polymeric matrices [1]. However, the carbonaceous nature of carbon fibre surface leads to low levels of stress transfer from the matrix to the fibres. This lack of fibre–matrix adhesion has been partially overcome with the development of surface treatments that nowadays are implemented fully in the carbon fibre fabrication process [2]. But unfortunately, the conventional carbon fibre surface treatment used by manufacturers aims at polar structural resin such as epoxy resin. The carbon fibre surface treatment has not been

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studied in detail yet when the resin is non-polar structure, for example polyarylacetylene (PAA) resin.

PAA, as the matrix for high temperature composites of the next generation, has been investigated owing to its outstanding heat resistance and excellent ablative properties [3]. PAA is a kind of high performance resin made up of non-polar structural ethynyl aromatic hydrocarbons, which can be cured to a highly cross-linked aromatic polymer that contains only carbon and hydrogen by means of addition polymerization without any elimination of low molecules such as water. PAA has advantages over other state-of-the-art phenolic resin system because of its ease of processability, smaller hygroscopic coefficient, lower pyrolysis shrinkage and higher char yield [4]. It is well known that the fibre–matrix interfacial properties play an important role in manipulating the macroscopic properties of fibre reinforced polymer composites [5]. Fibre–matrix adhesion is important in achieving efficient stress transfer from the matrix to the fibres. However, the nature of the structure and chemical inertness of carbon fibre and the non-polar structure of PAA result in weak interaction and perform a poor bonding behaviour in composites. Thus, the adhesion between carbon fibre and PAA resin can hardly come to an ideal prospective aim, which results that the outstanding heat resistance and excellent ablative property of PAA can not be materialized. It is quite necessary to improve the interfacial performance of CF/PAA composites.

One of the methods improving the interfacial properties is to modify the carbon fibre surface, for example, chemical oxidation [6], anodic oxidation [7–9], ozone oxidation [10], plasma oxidation [11, 12], activating the surface of carbon fibres [13] etc. But all the methods were developed against the polar resin, such as epoxy, phenolic resins. There are a few modifying methods aiming at non-polar resin [14]. And the produced polar groups such as hydroxyl and carboxyl on the carbon fibre surface during surface treatment process are usually not fit for the non-polar structural PAA resin. The other methods are sizing or coating treatment [15, 16] to improve the interfacial properties. In practice, carbon fibres are produced mainly as the reinforcement of polar resin, especially epoxy resins. For this purpose, the fibres are sized or coated during the produce program. It has to be assumed that the sizings or coatings are optimized in relation to epoxy resin matrix. The sizing or coating on carbon fibre surface is not agree with the non-polar structural PAA resin though the problem or role of them used in the manufacturing of carbon fibre reinforced PAA composite has not been discussed in the published literature.

In present work, in order to obtain the more ideal interfacial properties of the composites and then to further understand the interfacial behavior and the mechanism of increasing the fibre–matrix interfacial adhesion, the organic–inorganic hybrid nanocoatings, silsesquioxane (SSO), are used to treat carbon fibres. SSOs are excellent heat resistance materials. The name of SSO derives from the non-integer (one and one-half or sesqui) ratio between oxygen and silicon atoms and the organic substituent [17]. SSO refers as one kind of compound that contains a silicon–oxygen nanostructural skeleton with intermittent siloxane chains (general formula $\text{RSiO}_{1.5}$), R is H, alkyl, alkylene, aryl, aromatic alkylene or their derivative groups [18], which are reactive or inertial functional groups. SSO has several structural types such as random, ladder, cage and semi-cage structure. SSO can be prepared through the hydrolytic condensation of the precursor of the organic siloxane ($\text{RSi}(\text{OR}')_3$, R and R' are different organic groups [19]. SSO with cage structure is also called polyhedral oligomeric silsesquioxanes (POSS, or $(\text{RSiO}_{1.5})_n$, where $n = 6, 8, 10, \dots$), as a new chemical feedstock technology for the preparation of organic–inorganic hybrid materials [20]. Literatures concerning incorporating dispersed SSO into traditional organic polymer systems have been published and the amount of them increases year by year. Those researches have prepared new hybrid inorganic–organic polymer systems with remarkable enhancements in mechanical and physical properties including dramatic increases in both glass transition and decomposition temperatures [21, 22], reduced flammability [23], increased moduli [24, 25] and oxidation resistance [26, 27]. SSO with appropriate functional groups, active (methacryloxy)propyl groups, was chosen and used as carbon fibre surface coating according to the structure of PAA resin. The effects of coating structures on the mechanical interfacial properties of CF/PAA composites were investigated in most detail.

Experimental

Materials

PAA resin used for the fabrication of all composites in this study was supplied by Aerospace Research Institute of Material & Processing Technology (China). Poly(acrylonitrile) (PAN) precursor carbon fibers (3×10^3 single filaments per tow, tensile strength was 3.38 GPa, average diameter was $7 \mu\text{m}$, density was 1.76 g cm^{-3} , linear mass was 0.161 g m^{-3}) was obtained from Jilin Carbon Co. (China). [3-(methacryloxy)

propyl]trimethoxysilane (MPMS), which was the precursor of hydrolytic condensation, acquired from Nanjing Shuguang Coupling Agent Factory (China) and used as received. MPMS-SSO was synthesized by hydrolytic condensation method from MPMS. (methacryloxy)propyl polyhedral oligomeric silsesquioxane (Methacryl-POSS) (T_8 , as shown in Fig. 5d) was bought from Hybrid Plastics Co. (US). Most of the chemicals used in this study, including analytically pure ethanol (C_2H_5OH), formic acid ($HCOOH$), acetone, and tetrahydrofuran (THF), were purchased from the Tianjin First Factory of Chemical Agents (China) and the distillations of them were used if necessarily.

Methods

Synthesis of MPMS-SSO

The hydrolytic condensation of MPMS was carried out in beakers placed in a water bath, using C_2H_5OH and $HCOOH$ in a molar ratio of $OH/Si = 3.2$ and $HCOOH/Si = 3-6$, stirring. The process of the reaction was performed in three steps. Firstly, the plastic films were used to seal the beakers for 7 days, then several small holes of needle size were made on the films for another 2 days and finally open the beaker for several days until it come into being viscoelastic state. The temperature of bath was controlled under $50\text{ }^\circ\text{C}$. The product was a mixture of cage structure SSO (T_6 , T_8 , T_{10} , T_{12} etc.) and ladder structure SSO, which will be proved in next section.

MPMS-SSO characterizations

Fourier transform infrared (FT-IR) spectra of MPMS and MPMS-SSO were measured with a spectral resolution of 4 cm^{-1} on a Nicolet Nexus670 FT-IR spectrophotometer by attenuated total reflection (ATR) method at room temperature.

Nuclear magnetic resonance (NMR) spectroscopy was carried out with a Bruker AV 400 instrument (Bruker, Switzerland). Syntony frequencies of 1H , ^{13}C and ^{29}Si were 399.95, 100.85 and 79.45 MHz, respectively; syntony widths were 4.25, 25.06 and 25.06 kHz; pulse angles wear 6.5, 2.8 and 7.2 s; pulse intervals were 9.33, 1.06 and 1.35 s; numbers of syntony were 8, 1311 and 3395; dimethyl sulfoxide ($DMSO-d_6$) was used as solvent to detect OH groups.

Mass spectra were obtained with a Biffex III UV-MALDI-TOF Mass Spectrometry (Bruker, Billerica), equipped with delayed extraction, a multisample probe, a TOF reflection analyzer, a pulsed nitrogen laser with wavelength 337 nm and pulse width 3 ns,

and a linear flight path length of 1 m. The flight tube was evacuated to 10^{-5} Pa. All the measurements were performed in reflection mode and positive ion detection potential 20 kV, the delayed extraction potential was 14.5–17 kV, and the delay time was 50–200 ns; 10–50 single-shot signals were accumulated for each spectrum. Mass calibrations were performed externally, and samples were diluted to 0.25 kg m^{-3} and measured in the matrix of a negative ion mode, employing angiotensin II and bovine insulin b-chain (oxidized).

Carbon fibre surface treatments and preparation of CF/PAA composites

The 2 wt.% THF solutions of coating were prepared for the coating treatment of carbon fibre surface. Carbon fibre coating treatment method was shown in Fig. 1. The unidirectional long carbon fibre reinforced PAA composites were made with both untreated and treated carbon fibres. The lamination process for the unidirectional composite was followed. CF was wound on a square hob and the number of circle was recorded for calculating the content of the resin. The resin was heated for several minutes at $45\text{ }^\circ\text{C}$, dumped onto fibres and kneaded by hand until it became uniform. Curing was performed in a compression moulding machine by the method of compression moulding, and the content of the resin in composites was controlled at about 35 wt.%. The curing process was shown as follows, $120\text{ }^\circ\text{C}$ for 2 h, $140\text{ }^\circ\text{C}$ for 2 h, $180\text{ }^\circ\text{C}$ for 2 h, $200\text{ }^\circ\text{C}$ for 2 h, and $250\text{ }^\circ\text{C}$ for 0.5 h. During the curing process, the pressure was 2 MPa, which was loaded after the temperature being increased to $120\text{ }^\circ\text{C}$ and kept for 20 min, and was kept in other temperature steps. When the curing process had been finished, the mould was cooled to room temperature with the pressure being maintained. All composite samples were 200 mm in length 6 mm in width and 2 mm in thickness.

Interfacial characterization of CF/PAA composites

Interlaminar shear strength (ILSS) of CF/PAA composites was tested on an universal testing machine

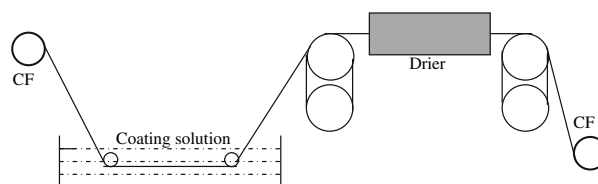


Fig. 1 Schematic process of CF coating treatment

(WD-1, Changchun, China) using a three point short beam bending test method according to ASTM D2344 standard. Specimens were cut and the dimensions were 20 mm × 6 mm × 2 mm, with a span to thickness ratio of 5. The condition of the specimen and an enclosed space where test was conducted was maintained at room temperature. The specimens were tested at a rate of cross-head movement 2 mm/min. ILSS, Γ , for the short-beam test was calculated according to the following equation

$$\Gamma = \frac{3P_b}{4bh} \quad (1)$$

where P_b is the maximum compression load 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 reported was the average of more than 8 successful measurements.

S4700 scanning electron microscopy (SEM, Hitachi Co., Japan) was used to observe the shear fracture topographies of CF/PAA composites. Due to the poor conductivity of the coating on carbon fibres, the samples were metallized with a thin layer of Pt, 10 nm in thickness.

Results and discussions

Structure of MPMS-SSO

FT-IR of MPMS and hydrolytic condensation product (MPMS-SSO) was presented in Fig. 2. The band around 3410 cm^{-1} is assigned to the O–H stretching mode, and that in the 3700–2800 cm^{-1} region is due to

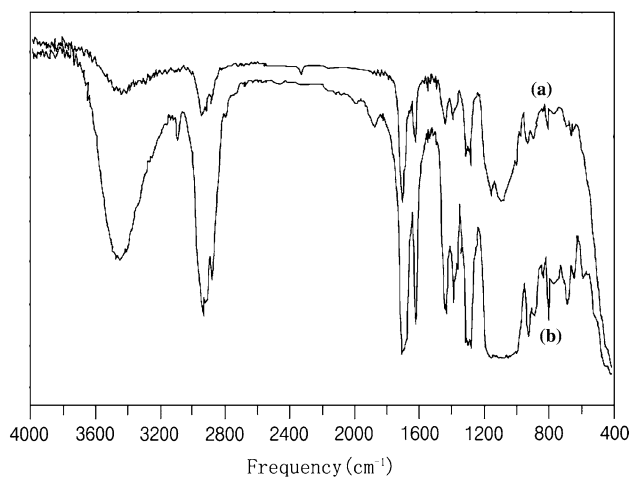


Fig. 2 Original materials (MPMS) FTIR spectrum (a) and the spectrum of the products (MPMS-SSO) condensed at 35 °C in 10 days (b)

the hydrogen bonding with the residual bound water. The peaks at 3110 and 1409 cm^{-1} , respectively, originate from the C=C–H and C=C stretching. The free carbonyl peak appears at 1711 cm^{-1} and the peak at 1282 cm^{-1} is associated with the ester functionality of MPMS. The peak at 1080 cm^{-1} is assigned to the Si–O–CH₃ bending. The MPMS-SSO presents the characteristic MPMS peaks (3110, 1409, 1711 and 1282 cm^{-1}), as shown in Fig. 2b. On the other hand, the Si–OH stretching vibration (950 cm^{-1}) in SSO, a fingerprint of uncondensed Si–OH group, is sometimes referred to as a defect band within the context of network structure. The Si–O–Si band (1150–1000 cm^{-1}) is strong, which indicate that hydrolytic condensation of MPMS takes place. This implies that the three-dimensional Si–O–Si network is formed by the hydrolytic condensation of MPMS.

Figure 3 presents NMR data of MPMS-SSO. As shown in Fig. 3(a), ¹H NMR spectra data (ppm) for the peaks of H protons in the groups: 0.698 (attached to the carbon adjacent to the silicon groups); 1.784 (attached to the second carbon from the silicon groups), 1.925 (attached to the carbon adjacent to the double bonds); 3.433, 3.450 (methyl protons of methanol); 4.103, 4.111 (attached to the distal and the proximal carbon of the ether groups); 5.545, 6.091 (attached to the double bonds, =CH₂); 7.283 (Si–OH). The DMSO-d₆ is given by 2.887–2.972. Figure 3(b) shows ¹³C NMR spectra data (ppm) for the peaks of C atoms in the groups: 8.354 (attached to Si), 17.865 (–CH₃), 21.945 (the middle carbon in –CH₂CH₂CH₂); 66.121 (the proximal carbon of the ether groups in –CH₂CH₂CH₂); 125.006 (=CH₂); 135.983 (the proximal carbon of the ether groups in double bonds) and 167.019 (–COO–). These data are well in an agreement with that of ¹H resonances and give complementary information for the characterization of the structure. The ²⁹Si NMR spectrum of the MPMS-SSO is reported in Fig. 3(c). The peak at –56.577 ppm is due to Si atoms with only one Si–O–Si bond, the peaks at –65.681 ppm correspond to Si atoms with two Si–O–Si bonds (or to Si atoms with three Si–O–Si bonds in strained cycles), and the peak at –114–121 ppm corresponds to Si atoms with three Si–O–Si bonds.

Figure 4 shows MALDI-TOF mass spectra of the condensed products MPMS-SSO. All peaks in the $m/z = 630$ –3000 Da range correspond to the oligomers derived from the hydrolytic condensation, and the proposed formulas corresponding with the peak data are assigned as shown in Table 1. They are only one of the multi-structural ones, and might not be the optimum one. Assigned with the generic formula (RSiO_{1.5})_n, (RHSiO_{1.5-x/2n})_n(OH)_x, (RSiO_{1.5-y/2n})_n(O-

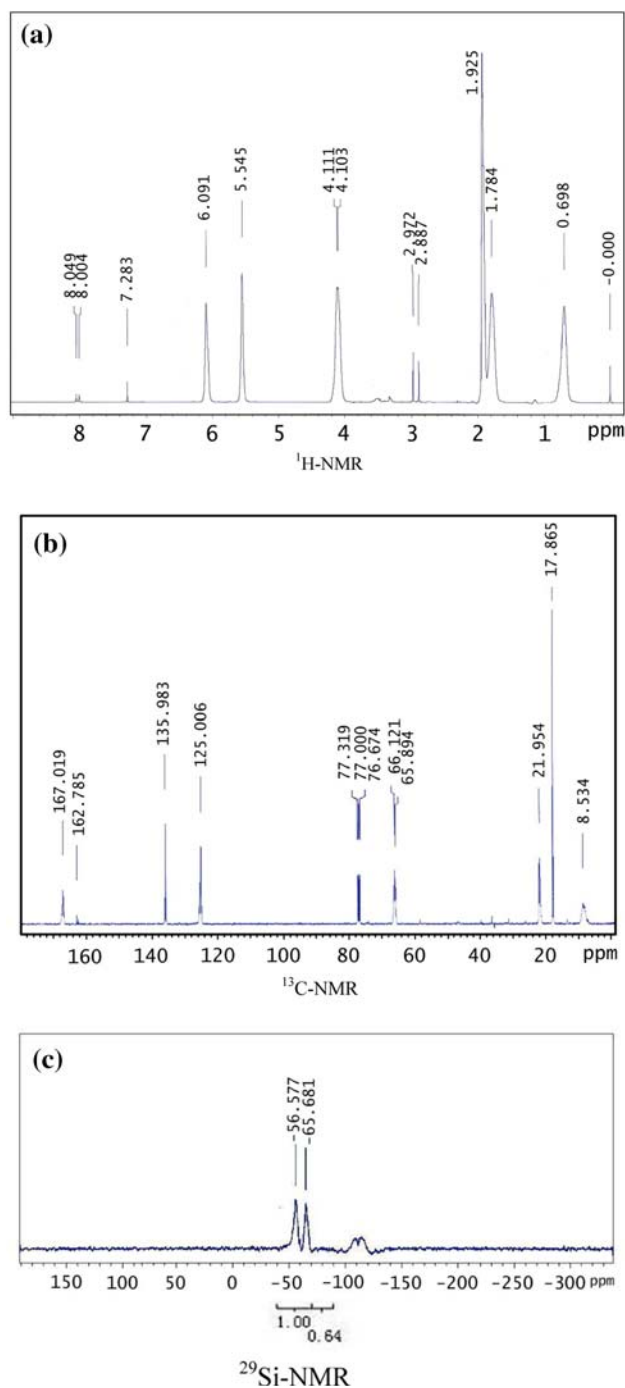


Fig. 3 NMR spectrum of MPMS-SSO. (a) ^1H -NMR. (b) ^{13}C -NMR. (c) ^{29}Si -NMR

CH_3)_y or $[\text{RSiO}_{1.5-(x+y)/2n}]_n(\text{OH})_x(\text{OCH}_3)_y$ (R is $-(\text{CH}_2)_3\text{OOC}(\text{CH}_3)\text{C}=\text{CH}_2$; $n = 1, 2, \dots$; $x, y = 1, 2, \dots$), they have an excellent compliance among their molecular weights, according to ion adducts $[\text{M} + \text{H}^+]$, $[\text{M} + \text{Na}^+]$ and $[\text{M} + \text{K}^+]$, and experimental ones.

According to the results of FT-IR, NMR (^1H , ^{13}C and ^{29}Si) and MALDI-TOF mass spectra, the components of MPMS-SSO and the structure of each component

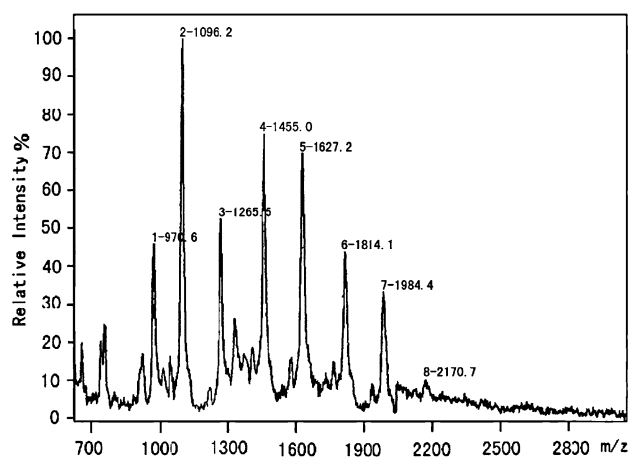


Fig. 4 MALDI-TOF mass spectra of the condensed products MPMS-SSO

Table 1 Assignments of MPMS-SSO formulas based on MALDI-TOF mass spectra

m/z (Experimental.)	Assignments ($+\text{Na}^+, \text{H}^+, \text{K}^+$)	m/z (Predicted.)
970	$\text{T}_3(\text{OCH}_3)(\text{OH})_2$	976
1096	T_6	1097
1265	$\text{T}_6(\text{OCH}_3)_7(\text{OH})$	1267
1455	T_8	1455
1627	$\text{T}_8(\text{OCH}_3)_7(\text{OH})$	1625
1814	T_{10}	1813
1984	$\text{T}_{10}(\text{OCH}_3)_7(\text{OH})$	1983
2170	T_{12}	2171

T is $\text{CH}_2=\text{CH}(\text{CH}_3)\text{COO}(\text{CH}_2)_3\text{SiO}_{1.5-(x+y)/2n}$

can be acquired. Some typical structures, including ladder, cage and others, were presented in Fig. 5. Every one is organic-inorganic hybrid structure that is made up of C–C organic chains and Si–O–Si inorganic core. Those hybrid structures have important effects on the adhesion and interaction between fibres and PAA resin when MPMS-SSO was used as coating to treat carbon fibre surface.

Interfacial properties of CF/PAA composites

Three kinds of coatings, MPMS (the structure is shown in Fig. 6), MPMS-SSO (the structure is shown in Fig. 5) and Methacryl-POSS (T8, as shown in Fig. 5 d), were used to treat the surface of carbon fibres. ILSS of CF/PAA composites were shown in Fig. 7. ILSS of untreated CF/PAA composites was only 30.2 MPa which indicated there was a weak bonding between fibres and PAA resin. The carbonaceous nature of fibre surface and the non-polar aromatic structure of PAA result in weak interaction between fibres and PAA

Fig. 5 Some typical structures of MPMS-SSO (R is –(CH₂)₃OOC(CH₃)C = CH₂)

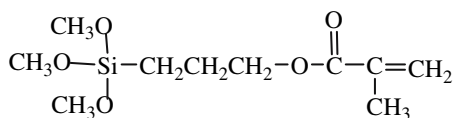
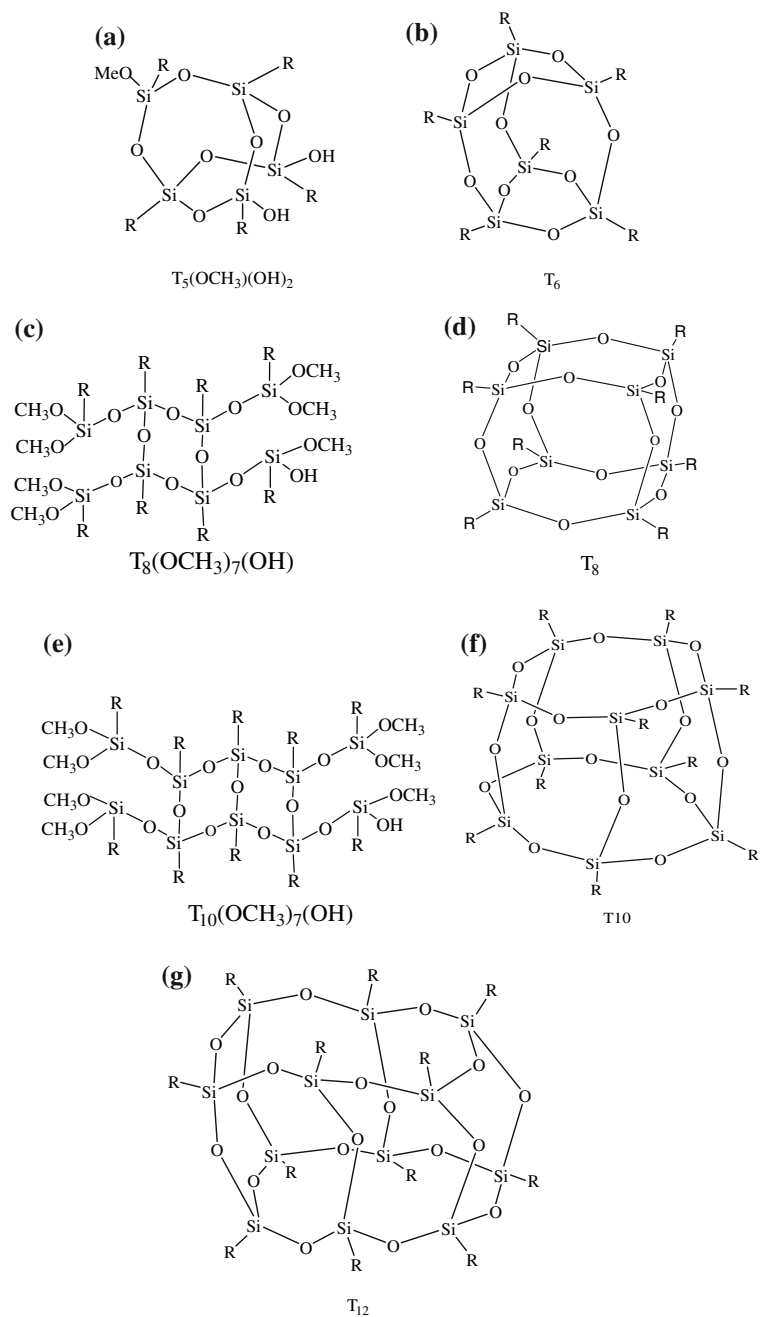


Fig. 6 Structure of MPMS

resin. ILSS of CF/PAA composites treated with MPMS coating was increased by 8% to 32.6 MPa while those of CF/PAA composites treated with MPMS-SSO and Methacryl-POSS coatings were increased by 34% and 42% to 40.5 MPa and 42.9 MPa, respectively. SEM

micrographs of the shear fracture of CF/PAA composites were presented in Fig. 8. Figure 8(a) showed the fracture of untreated CF/PAA composite. Long carbon fibres in untreated composites were pulled out, and the surface of carbon fibres was clean, almost no resin was remained on the surface. After being treated with MPMS coating (Fig. 8(b)), quantities of fibres were still pulled out but the pull-out length was shorter than that of untreated. There was a little resin on the surface of carbon fibres. After being treated by MPMS-SSO coating (Fig. 8(c)), many fibres were still pulled out and there was a bundle of fibres which were embedded

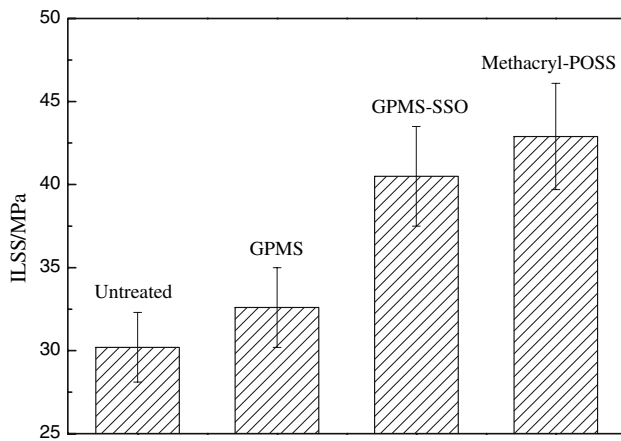


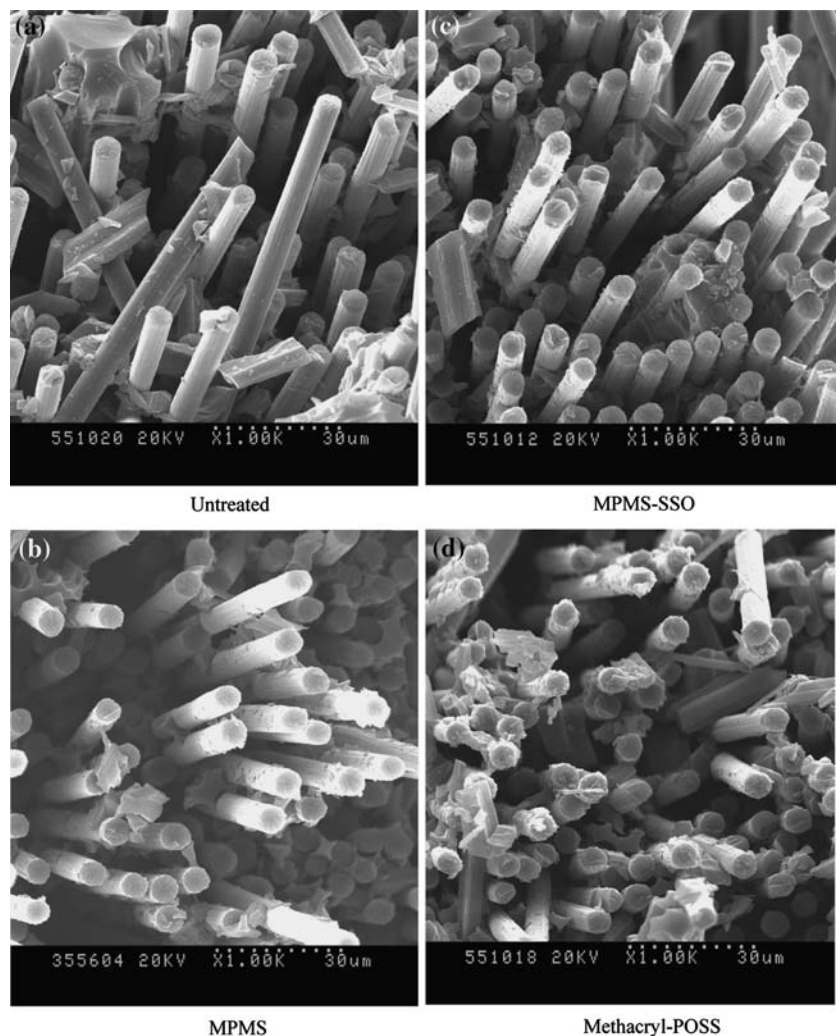
Fig. 7 ILSS of untreated and MPMS, MPMS-SSO and Methacryl-POSS coating treated CF/PAA composites (the concentrations of all solutions are 2 wt.%)

in resin although microdebonding still occurred between carbon fibres and PAA resin. Figure 8(d) showed the shear fracture of the Methacryl-POSS

coating treated CF/PAA composites. The number of bundle was increased and the length of pulled fibres became shorter. All results mentioned above, including ILSS and SEM micrographs, suggested that the sequence of treatment effect is Methacryl-POSS followed with MPMS-SSO and the last one is MPMS. Methacryl-POSS could sharply build up the interfacial bonding and improve the mechanical interfacial properties of CF/PAA composites.

The interaction between fibres and coatings was physical process and that between coatings and PAA resin was chemical reaction because there were chemical bonds formed by double bonds in coatings during the cure process of PAA. The nature of physicochemical interaction between carbon fibres and PAA resin through coatings on fibre surface in composites treated with different structural coatings was the same. Thus, the difference of structure led to the different treating effects among MPMS, MPMS-SSO and Methacryl-POSS coatings. The molecular weight of

Fig. 8 SEM micrographs showing the shear fracture of CF/PAA composites (a) untreated and treated by 2 wt.% MPMS (b), MPMS-SSO (c), Methacryl-POSS (d) coating solutions



MPMS-SSO was larger than that of MPMS and the structure of MPMS-SSO was more complicated than that of MPMS. The structural types of MPMS-SSO were various, including ladder, cage and random structure while Methacryl-POSS is cage compounds. The ILSS of Methacryl-POSS treated composites was the largest among the three kinds of coating treated composites. The nano cage structure of Methacryl-POSS is helpful to distribute the load and transfer it from PAA rein to CF. Thus, the cage structure is the most important factor which influences the mechanical interfacial property of CF/PAA composites when functional groups were same.

Conclusions

[3-(methacryloxy)propyl]silsesquioxane (MPMS-SSO) can be obtained from the hydrolytic condensation of [3-(methacryloxy)propyl]trimethoxysilane (MPMS). The complicated structure, including both proposed cage and ladder one, of MPMS-SSO may be assigned by FT-IR, NMR (^1H , ^{13}C and ^{29}Si) and UV-MALDI-TOF MS. The values of ILSS of CF/PAA composites untreated and treated with different coatings (MPMS, MPMS-SSO and Methacryl-POSS) show that the Methacryl-POSS coating has the best effect on the interfacial properties and the MPMS-SSO coating treatment effect is the second, which also be proved by the SEM topographies of shear fracture of CF/PAA composites treated with different coatings. The cage structure of Methacryl-POSS has is the most important factor which influences the mechanical interfacial properties of CF/PAA composites. The organic-inorganic hybrid polymorphic MPMS-SSO has better treating effect than simple MPMS siloxane. The results suggest that the structure of coating is important when using coating to treat fibre surface for build up the adhesion and improving interfacial properties of fibre reinforced polymer matrix composites.

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