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Controlled interface between carbon fiber and epoxy by molecular self-assembly method

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Abstract

In this paper, a new treatment method based on molecular self-assembly on carbon fiber surface was proposed for obtaining a controlled interface between carbon fiber and epoxy matrix in composite system. To form the controlled interfacial region, the surfaces of carbon fibers were first metallized by electroless Ag plating, then were reacted with a series of thiols (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. The morphology, structure and composition of untreated and treated carbon fiber surface were investigated by atomic force microscope (AFM), surface-enhanced Raman scattering spectroscopy (SERS) and X-ray photoelectron spectroscopy (XPS), respectively. SERS study showed that thiols chemisorbed on Ag/carbon fiber in the form of thiolate species via the strong S–Ag coordinative bond. XPS study further confirmed the chemisorption by an S $2p_{3/2}$ component observed at 162.2 eV. The binding energy was characteristic of silver thiolate. The interfacial shear strength of the carbon fiber/epoxy microcomposites was evaluated by the microbond technique. The results showed that there was a direct effect of the interfacial parameters changes such as chain lengths and surface functional groups on the fiber/matrix adhesion.

Keywords: Composites; Self-assembly; Raman spectroscopy and scattering; Interfacial adhesion

1. Introduction

Interfacial adhesion plays an important role in determining the mechanical properties of composites, especially carbon fiber/epoxy composites. Carbon fibers, without any surface treatment, cause a weak adhesion to the matrix resin. Consequently, a variety of surface treatments of carbon fibers are developed such as oxidation, coating, grafting [1–6], etc. All surface treatments enhance the interfacial shear strength (IFSS) by introducing chemically active groups on the fiber surfaces which increases the reactivity with the matrix, enhancing surface roughness to produce better mechanical interlocking as well as increasing the surface energy for improved wetting. However, it is not yet fully understood how these surface treatments ultimately influence the interfacial properties because of the difficulties in quantitatively defining and controlling both the interfacial thickness and surface distribution of organic functional groups on carbon fibers. So, there is an urgent need for searching for an appropriate method which can simplify and model various complex interfaces to gain a better insight into the interfacial action mechanisms.

Molecular self-assembly provides a means to obtain a controlled and ordered structure. Self-assembly monolayers (SAMs) are usually prepared by organic molecules in solutions spontaneously chemisorbed on solid substrates with a strong coordinative bond via sulfur atom and formed a closely packed and highly ordered monolayers by the van der Waals interaction among the molecules [7–10]. The objective of this study is to introduce such assembly method into interface between carbon fiber and epoxy matrix for controlling interfacial thickness and density, organized arrays of functional groups at the molecular level [11]. Although self-assembly monolayers (SAMs) systems have occupied a wide range of applications in the fields of biology, microelectronics, optics and coatings [12–14], its studies in composite systems have been less frequently reported. Lu et al. [15] have investigated in detail the organic heterocyclic compounds containing nitrogen or sulfur atoms as self-assembly thin films in aluminum powder/polyurethane composites. They found the treated aluminum powder-reinforced PU composites possessed a higher tensile

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strength and higher elongation than those of the untreated systems. To our knowledge, no studies concerning SAMs at carbon fiber/epoxy interface have been considered so far.

In this paper, the method proposed mainly consists of the following steps: (a) the electroless Ag plating of the carbon fiber surfaces; (b) the formation of terminally functionalized alkanethiols or aromatic thiols SAMs on Ag-plated carbon fiber surfaces; (c) the generation of the strong adhesion interface layer in modified carbon fiber/epoxy composite. Atomic force microscopy (AFM) was used to observe the morphology of carbon fiber before and after modification. We examined the adsorption behavior of thiols SAMs on Ag-plated carbon fiber by surface-enhanced Raman scattering spectroscopy (SERS) and X-ray photoelectron spectroscopy (XPS). The interfacial shear strength (IFSS) values of microcomposites were obtained using the microbond test.

2. Experimental

2.1. Raw materials

The resin system used in this study consisted of three components, epoxy EPO 1441-30 as the resin, acid anhydride as the curing agent, and *N*,*N*-dimethyl benzyl amine as the accelerating agent, in ratio of 100:70:1 by weight. All these components were supplied by Shell Chemical Corporation. The fibers used in the paper were polyacrylonitrile based carbon fibers, which were 1K, high strength type, provided by Jilin Carbon Factory, China.

The main chemicals used in this study were 2-mercaptoethanol ($HO(CH_2)_2SH$, denoted later as 2-MEOL, 99% purity), 6-mercapto-1-hexanol ($HO(CH_2)_6SH$, 6-MHOL, 97%), 11-mercapto-1-undecanol ($HO(CH_2)_{11}SH$, 11-MUOL, 97%), 4-aminothiolphenol ($H_2N(C_6H_4)SH$, 4-ATP, 96%), and 4-hydroxythiophenol ($HO(C_6H_4)SH$, 4-HTP, 99%). They were purchased from Aldrich Chemical Co. and used as received without further purification. The solvents (acetone, ethanol) and other chemicals were of reagent grade.

2.2. Electroless silver plating on carbon fiber surface

Prior to use, the fiber surface was extracted for 48 h with acetone in order to remove epoxy sizing. The Ag plating bath was composed as following: 3.5 g of $AgNO_3$, sufficient NH_4OH to dissolve precipitates, 15 g of NaOH, 4.5 g of glucose, 4 g of tartaric acid, 100 ml of ethanol and 900 ml of H_2O [16]. Before being plated, bundles of carbon fibers were rinsed with basic solutions, etched with sulfuric acid, sensitized with stannum dichloride ($SnCl_2$) and activated with palladium chloride ($PdCl_2$) solutions. Then fibers were dipped into the plating bath for 2 min. Finally fibers were washed several times with deionized water and ethanol.

2.3. Preparation of self-assembled monolayers (SAMs) on Ag/carbon fibers

The Ag-plated carbon fibers were separately immersed into 0.5 mM solutions of five thiols in ethanols for approximately 24 h at room temperature. After the modification, the fibers were rinsed thoroughly, first with pure ethanol and then with deionized H_2O in order to clean the surface from residues of the modification solution, then dried with a stream of nitrogen gas. There was a delay of three days between the preparation and XPS measurement of SAMs/Ag/carbon fiber samples. During this period, the samples were kept in a sealed container and protected from exposure to light and dust.

2.4. Atomic force microscope (AFM) observation of carbon fiber surface

The morphology of carbon fiber surface before and after modification was examined using a Solver P47 atomic force microscope made in Russia NT-MDT Corporation. All images were obtained in the noncontact mode at room temperature. The scanning scope was $2\,\mu m \times 2\,\mu m$. The AFM images were displayed with different shades of grey (dark grey indicating lower parts and light grey higher parts of the surface).

2.5. SERS measurement of SAMs on Ag/carbon fiber

SERS spectra of SAMs on Ag-coated carbon fiber were obtained with a T64000 Raman spectrometer from France JY Company equipped with liquid nitrogen-cooled CCD detector and an Ar^+ gas laser (514.532 nm). The Raman band of a silicon wafer at $520\,cm^{-1}$ was used to calibrate the spectrometer. The laser power at the sample was 200 mW. The spectral resolution was $0.15\,cm^{-1}$. The scattered light was at an angle of 180°.

2.6. XPS measurement of SAMs on Ag/carbon fiber

XPS measurements were performed utilizing a VG ESCALAB MK II photoelectron energy spectrometer. The spectra were collected using an Mg Kα X-ray source (1253.6 eV). The binding energy scale was calibrated by setting the Ag $3d_{5/2}$ peak of bulk metals to values 368.26 eV. The X-ray power and take-off angle of the photoelectron were set at 200 W and 45°, respectively.

2.7. Testing of interfacial shear strength of modified carbon fiber/epoxy composites

A microbond test was performed to evaluate the interfacial shear strength (IFSS) between carbon fiber and matrix by pulling out a fiber from cured epoxy resin droplet. The composite specimens were prepared by dipping epoxy resin droplets on carbon fiber monofilament with the embedded length of 60–80 μm using a fine-point applicator. The specimens were cured at 90 °C for 2 h, then cured at 120 °C for 2 h, and finally cured at 150 °C for 4 h. After this curing process, the single filament pull-out test was carried out on an interfacial microbond evaluation instrument, which was made by Tohei Sangyo Corporation of Japan. The pull-out test was performed at a crosshead displacement rate of $0.5\,\mu m\,s^{-1}$. The value of IFSS was calculated according to the equation

$$\mathrm{IFSS} = \frac{F}{\pi d l}$$

where F is the maximum load; d the diameter of the carbon fiber; l is the length of the fiber embedded in the resin. The recorded value of IFSS was calculated from the normal distribution of more than 100 successful measurements [17].

3. Results and discussion

3.1. AFM analysis of carbon fiber surface

The surface morphological changes of the treatment sample compared with untreated one were observed by AFM, as shown in Fig. 1. The scanning scope was $2\,\mu m \times 2\,\mu m$.

The surface morphology of untreated fiber is smooth and filled with a number of the strip grooves in the direction of the fiber length in Fig. 1a. When carbon fiber is metallized by electroless Ag plating, its surfaces become rough and is densely distributed even islands in Fig. 1b. That is to say, the original surfaces of the carbon fiber are completely and evenly covered by deposited Ag particles, which is favorable and significant for further self-assembly on Ag-plated carbon fiber, because organicsulfur molecules adsorb on carbon fiber via the combination of mercarpto groups with metal rather than carbon fiber. The morphology of SAMs treated Ag-plated carbon fiber is similar to Fig. 1b due to the fact that it is difficult to detect the monolayers within the large scanning scope.

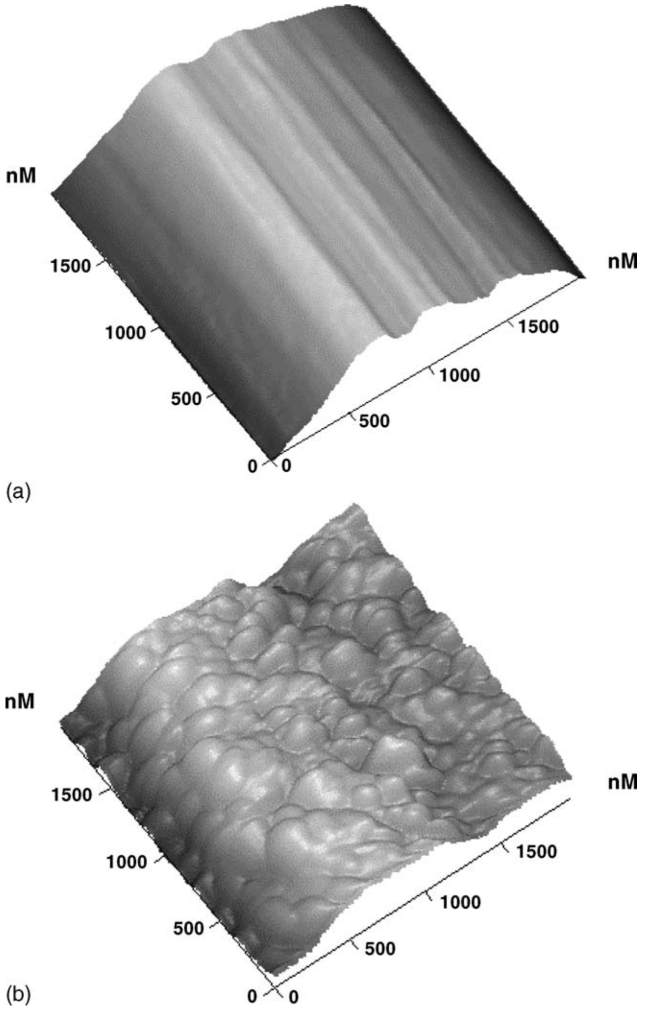

Fig. 1. AFM photographs of untreated (a) and treated (b) carbon fiber surface.

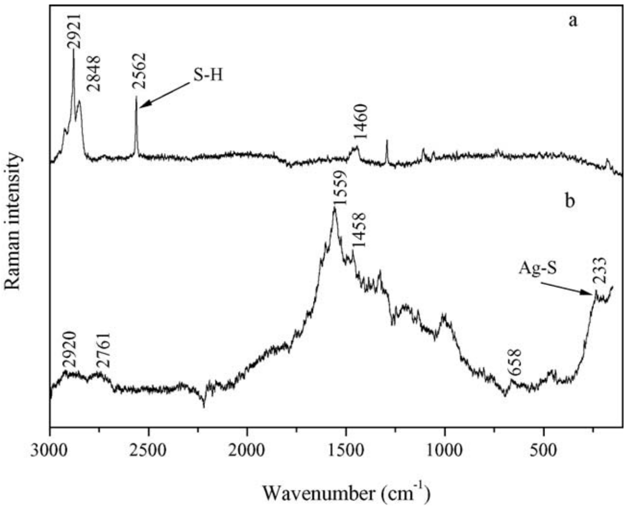

Fig. 2. Normal Raman spectrum of 11-MUOL (a) and SERS spectrum (b) of 11-MUOL adsorbed onto the Ag/carbon fiber substrate.

3.2. SERS analysis of SAMs on Ag/carbon fiber

Raman scattering signals of organic monolayers and submonolayers adsorption on the metal substrates such as Ag, Au and Cu with abundant roughness features can be significantly enhanced. In general, the most common substrates used for SERS are electrochemically etched electrodes, colloids and metal films vaccum deposited [18]. Usually, the electroless Ag plating as an active substrate can be also used for SERS study. In this work, the surface microstructures of the substituted alkanethiols and aromatic thiols molecules adsorbed onto the Ag-coated carbon fiber substrate by the electroless Ag plating were studied using SERS.

Fig. 2a and b shows the normal Raman spectrum of 11-MUOL solid and its SERS spectrum on the Ag/carbon fiber substrate, respectively. It is seen that the SERS spectrum is strikingly different from the solid, which indicates that only the adsorbed species are contributing to the intensity. In Fig. 2a, doublet peaks are observed at 2921 and 2848 cm^{-1}, attributed to the asymmetrical and symmetrical –CH_2 stretching vibration modes of 11-MUOL. By comparison, the doublet peaks are dramatically attenuated in the intensity in Fig. 2b. This means the C–H stretching modes are parallel to the Ag–carbon fiber substrate according to the SERS selection rules [19,20]. That is, the polymethylene chain is almost perpendicular (or at least tilted) to the substrate surface, so, it can be concluded that 11-MUOL forms a standing-up phase on the surface. On the contrary, from Fig. 2a and b, the weak intensity and narrow peak in the vicinity of 1460 cm^{-1} band assigned to the –CH_2 bending vibration mode is dramatically enhanced and broaden. It is noted that strong Raman band of the S–H stretching vibration at 2562 cm^{-1} in Fig. 2a disappears in Fig. 2b, the missing S–H stretching band indicates the generation of the expected covalent bonding of the sulfur atoms to the Ag surface, which is demonstrated by the appearance of a new band at 246 cm^{-1} assigned to the Ag–S bond in Fig. 2b. That is to say, 11-MUOL species were chemisorbed onto the silver surface by the splitting of the S–H bond to form its thiolate. The comparison of the normal Raman spectra and its SERS spectra of 2-MEOL and 6-MHOL molecules are similar to those of 11-MUOL (not shown here).

The SERS spectra of self-assembly 2-MEOL, 6-MHOL and 11-MUOL monolayers ($(\mathrm{CH}_2)_n$, $n = 2, 6, 11$) with different alkyl chain lengths adsorbed onto the Ag/carbon fiber substrate are given in Fig. 3, where the new S–Ag bond stretching modes are observed at 215, 234 and 233 cm^{-1}, respectively. This indicates that three kinds of molecules reacted chemically with the silver surface via the formation of S–Ag bond. In addition, from Fig. 3a to c, it is observed that the relative intensity ratio of the band near 1458 cm^{-1} to the band of Ag–S bond increased gradually. In Fig. 3a, the relative intensity ratio is low; while the intensity ratio in Fig. 3b is comparative; Finally, the relative intensity ratio increases dramatically in Fig. 3c. This can be explained that with the increase of alkyl chain length, the number of methylene units increases, therefore, there is a significant increase in the relative intensity ratio. From another point of view, for $n = 2$ (a), the spectrum is completely dominated by the silver signal. The silver contribution decreases in a significant way for $n = 6$ (b). For $n = 11$ (c), the silver substrate does not disturb any more the spectral features of the monolayers as the overall shape of the

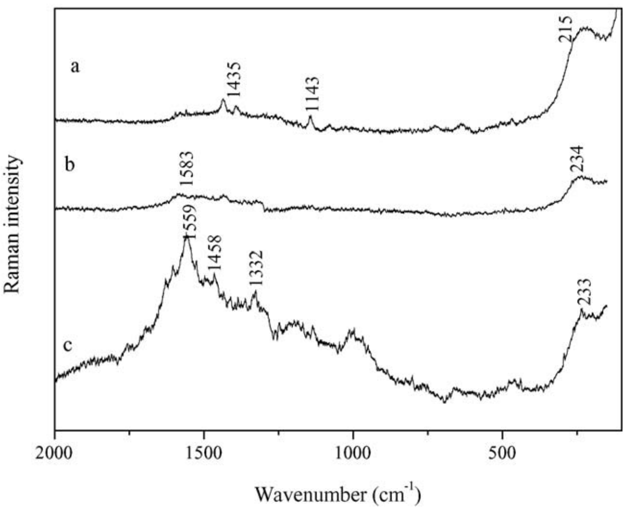

Fig. 3. SERS spectra of 2-MEOL (a), 6-MHOL (b) and 11-MHOL (c) adsorbed onto the Ag/carbon fiber substrate, respectively.

spectrum becomes independent of the chain length. The similar comparison on different chain length alkanethiolate/Au SAMs was presented in the literature [21].

Fig. 4 gives the normal Raman spectrum of 4-HTP and SERS spectrum of 4-HTP monolayers on Ag-coated carbon fiber. A special attention is paid to the latter region from 2500 to 3100 cm^{-1} range in the spectrum. A normal Raman spectrum of 4-HTP shows a strong peak at 2566 cm^{-1} attributed to the S–H stretching band, whose counterpart is completely absent after adsorption in Fig. 4b. This implies 4-HTP adsorbed on the Ag surface after losing its thiol proton. Meanwhile, the appearance of the new Ag–S band at 236 cm^{-1} indicates the chemical interactions between the sulfur atoms and the Ag surface. The 3059 cm^{-1} band in the NR spectrum is attributed to the ring C–H stretching band. Whereas the ring C–H stretching mode in the monolayer is almost absent in SERS spectrum. The rather abrupt change in intensity for ring C–H stretching band is understandable from SERS selection rules [22]. If the benzene ring of 4-HTP molecule is oriented perpendicularly with respect to the surface, the component of the polarizability tensor of the aromatic C–H stretching modes normal to the surface will be larger in magnitude. But if the benzene ring is parallel to the surface, the polarizability tensor will have only a very weak component perpendicular to the surface. Based on this argument, 4-HTP molecular plane is flat on the Ag/carbon fiber substrate. The another noteworthy point is that the in-plane C–C stretching mode of the benzene ring of 4-HTP is identified at 1600 cm^{-1}, we observed substantial difference in intensity of these bands in NR and SER spectra. Whereas it is strong in NRS, the intensity has decreased in SERS. This variation again could be interpreted in terms of SERS selection rules since this mode is along the molecular plane. The bandwidths of the benzene ring modes at 1596, 1529 cm^{-1} are broader than their counterparts in Fig. 4a, a direct surface-ring-π-orbital interaction might also be involved in the surface adsorption of 4-HTP on Ag/carbon fiber [23]. The SERS spectrum of self-assembly 4-ATP monolayers is similar to that of 4-HTP (not shown here).

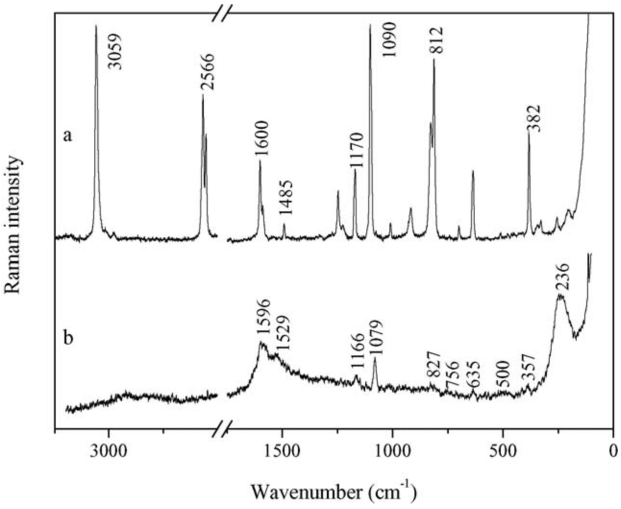

Fig. 4. Normal Raman spectrum of (a) 4-HTP and SERS spectrum and (b) 4-HTP adsorbed onto the Ag/carbon fiber substrate.

In line with the above Raman spectral studies, it is reasonable to propose that surface functionalized alkanethiols and aromatic thiols SAMs were chemisorbed onto the Ag/carbon fiber substrate through S atoms to form thiolated species. As expected, alkanethiols monolayers with different alkyl chain length covered the Ag/carbon fiber surface with –OH groups. Whereas aromatic thiols 4-ATP and 4-HTP monolayers were assembled on the Ag/carbon fiber substrate with a flat orientation.

3.3. XPS analysis of SAMs on Ag/carbon fiber

XPS is a well-established tool for the characterization of the molecular structure of organic films [21]. Fig. 5 provides the wide-scan XPS spectra of the untreated and treated carbon fibers. Comparing Fig. 5a and b, for the modified carbon fiber in the case of 2-MEOL SAMs, carbon, oxygen, sulfur and silver peaks are observable, which reveals the SAMs actually adsorbed on Ag/carbon fiber.

XPS has been widely used to characterize the attachment of the sulfur on the metal substrates [19,24,25]. Fig. 6 presents the deconvoluted peak of the S 2p spectrum from 2-MEOL SAMs on Ag-coated carbon fiber surface. The S 2p spectrum has a doublet structure with an area ratio of 1.3:1 and spin–orbit splitting of 1.2 eV. These peaks are assigned to the $2p_{3/2}$ and $2p_{1/2}$ spin–orbit split levels with binding energies of 162.2 and 163.4 eV, respectively. The majority of literatures [19,24,25] reported these binding energies were characteristic of thiolate species (CnS/Ag) and demonstrated the existence of a chemical metal–sulfur bond. However, the theoretical intensity ratio of 2:1 of the S2p doublet is not obtained exactly. The literature [19] suggested that deflection from an exact 2:1 intensity ratio might be indicative of oxidized sulfur species (S 2p binding energy above 166 eV) such as sulfonates. This means the emergence of a new peak corresponding to oxidized sulfur species causes the intensity loss of a thiolate species peak at 162.2 eV. In Fig. 6, a minor peak can be observed at 168.7 eV which implied the probable formation of SO_3–Ag bonds [16]. This oxygen-

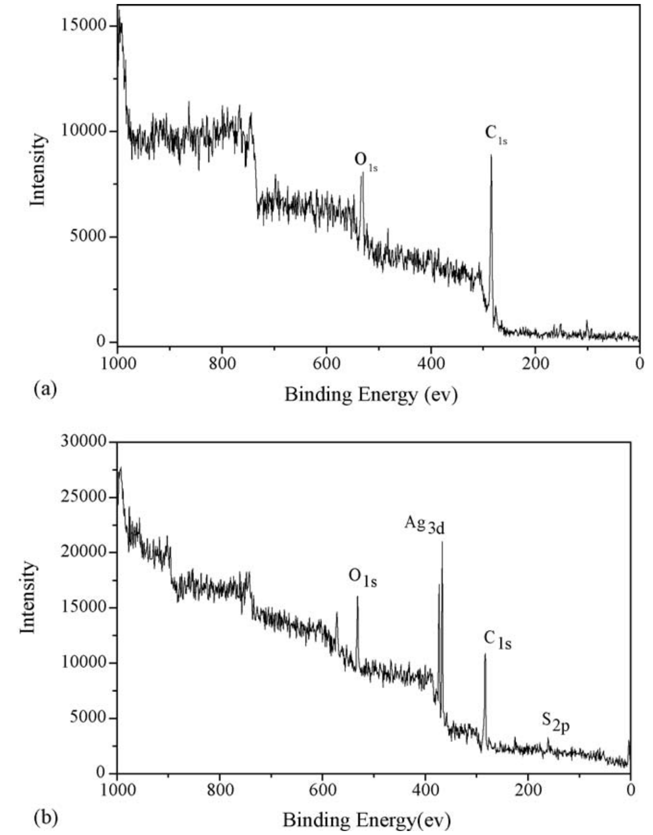

Fig. 5. XPS wide scan spectra of carbon fiber surface (a) before and (b) after modification with 2-MEOL self-assembly film.

containing sulfur species appears in the spectrum due to the fact that there was a delay between the preparation and measurement of the sample. No oxidized sulfur species are detected in the condition of the measurement performed immediately after the sample preparation [19]. From the above discussion, it is concluded that self-assembly organicsulfur molecules are actually chemisorbed on the Ag-coated carbon fiber surface through chemical bonds.

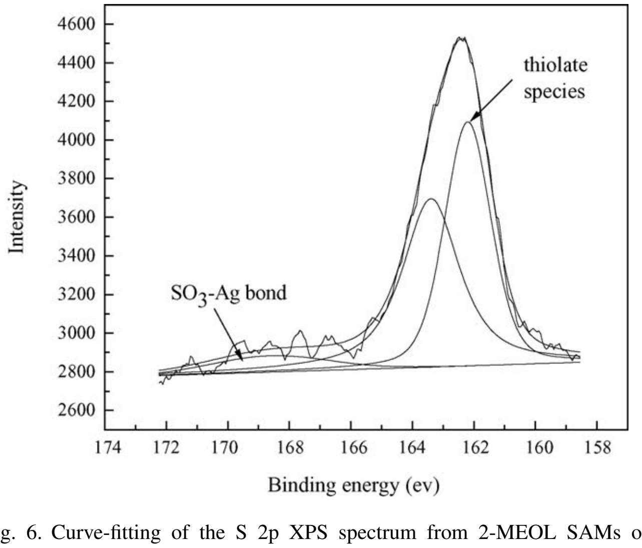

Fig. 6. Curve-fitting of the S 2p XPS spectrum from 2-MEOL SAMs on Ag/carbon fiber.

Table 1
IFSS values of untreated and treated carbon fiber/epoxy composites

	Carbon fiber		IFSS (MPa)
Before self-assembly		Untreated	30.66 ± 1.2
		Ag deposition	32.08 ± 1.6
After self-assembly	Alkanethiols	2-MEOL	33.15 ± 1.3
		6-MHOL	34.23 ± 1.4
		11-MUOL	36.04 ± 1.8
	Aromatic thiols	4-HTP	34.32 ± 1.5
		4-ATP	35.81 ± 1.6

3.4. IFSS analysis of carbon fiber/epoxy microcomposites

According to the normal distribution of more than one hundred successful measurements, the results of the interfacial shear strength (IFSS) of modified carbon fiber/epoxy composites compared to untreated composites are shown in Table 1. The results indicate that self-assembly monolayer treatment on carbon fiber surface improved the interfacial property of fiber/epoxy composite. Although their effects are obviously different, it appears that we can find certain relationship between the interfacial structures and properties.

Prior to self-assembly, the IFSS of Ag-plate carbon fiber composites is increased by 4.63%. Through the observation of the AFM, the main mechanisms responsible for the improvement of the interfacial shear strength are that the formation of Ag films on carbon fiber eliminates the defects of fiber surface, decreases the stress concentration, and increases fiber surface roughness (promoting the mechanical interlocking at the interface).

For hydroxyl substituted alkyl thiols SAMs, after Ag/carbon fiber surfaces are assembled with 2-MEOL, 6-MHOL, 11-MUOL, respectively, the IFSS values of composite samples all increase and are improved by 8.12, 11.64, 17.55% compared to untreated composite. They are chemisorbed onto Ag/carbon fiber through S atoms to form thiolate species, which has been proved by the analysis of SERS and XPS. Through SERS analysis, we have known molecules with different alkyl chain lengths had formed a standing-up phase on the surface. Therefore, the surface properties of carbon fibers were almost determined by the hydroxyl end-groups on SAMs surface. By the chemical interaction of the –OH end-groups and epoxy matrix, strong interfacial adhesion layers generated. Thus, SAMs/Ag were able to act as coupling agents between the carbon fibers and epoxy resin to enhance the interfacial adhesion. Moreover, the longer the alkyl chain, the higher the IFSS value. This may be explained due to the fact that SAMs with longer alkyl chain (strong van der Waals interaction between the alkyl chains) form higher-ordered and closer-packed structure, which results in more functional groups exposed on the entire system surface generating a better adhesion at the interface. Whereas the weak interaction between the alkyl short chains of 2-MEOL determines the less-ordered molecular packing with less functional groups exposed on outermost surface, which is the result of low IFSS values.

For aromatic thiols SAMs terminated with –OH, $-NH_2$, after Ag/carbon fiber surfaces are assembled with 4-HTP, and 4-

ATP, the IFSS values of composite samples all increase and are improved by 11.94, and 16.80%, respectively. They are also chemisorbed onto Ag/carbon fiber via S–Ag bond, which has been verified by SERS analysis in Fig. 4. Furthermore, according to the SERS selection rules, we have obtained that the benzene rings of 4-ATP and 4-HTP monolayers have a flat orientation with respect to the silver surface. From Table 1, it can be seen that the IFSS of 4-ATP treated carbon fiber composites increases by 16.8% compared to untreated composites and it has the better effect on the improvement of the interfacial property than that of 4-HTP. This significant difference may be because the $–NH_2$ group is more active than the –OH group towards the epoxy group of epoxy resin and as a result, causes a stronger chemical bonding with matrix.

From the above analysis, we only discussed the chemical bonding at the interface. In fact, it is assumed that when SAMs on carbon fiber surfaces have defects, the physical effects such as the entanglement between the SAMs alkyl chain and the polymer chain of the resin matrix may have contributions on the improvement of interfacial properties. The special attention is paid to the substrate quality for self-assembly process. In other words, the order of SAMs strongly depends on the quality of metal substrate. Generally, the best quality monolayers are prepared on the single-crystal metal substrates or evaporated metal films with atomically flat terraces. In this study, SAMs adsorbed on the electroless plating Ag substrate with large roughness observed with AFM in Fig. 1b. So, it is believed that there should be inevitable pits or depressions in SAMs.

As a result, the interfacial adhesion strength of the composites can be improved by controlling the interfacial microstructure parameters such as chain length and terminal groups. Especially, the effects of the longer alkyl chain and $–NH_2$ functional group on improving the interfacial properties were larger. The literature [26] reported that for alkanethiols SAMs, below 10 methylene units the monolayers was not densely packed whereas above 22 methylene units the monolayer was not well-defined. So, SAMs with the longer chain until 22 methylene units will be considered for this study.

4. Conclusions

A new method based on the self-assembly technique was proposed to obtain a controlled interface in carbon fiber/epoxy composites in this paper. We chose alkanethiols with different alkyl chain length 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 organic-sulfur compounds chemisorbed onto the Ag-coated carbon fiber 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 reinforced by treated carbon fibers with 2-MEOL, 6-MHOL and 11-MUOL SAMs increased by 8.12, 11.64, 17.55%, respectively. 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, the higher the IFSS. This is because the longer alkyl chain molecules formed a more closely packed structure with more active functional groups exposured at the outermost surface. The IFSS of 4-ATP and 4-HTP treated carbon fibers composites increased by 11.94, and 16.80%, respectively. It can be concluded that the effects of functional groups on the interfacial properties were larger due to the higher reactivity of $–NH_2$ groups toward the epoxy than that of –OH groups.

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