Effects of Chain Lengths, Molecular Orientation, and Functional Groups of Thiols Adsorbed onto CF Surface on Interfacial Properties of CF/Epoxy Composites

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ABSTRACT: In this article, a new treatment method based on molecular self-assembly on carbon fiber (CF) surface was proposed for obtaining a controlled interface between CF and epoxy matrix in composite system. To form the controlled interfacial region, the surfaces of CF were first metallized by electroless Ag plating, then were reacted with a series of thiols (alkanethiols, aromatic thiol, and heterocyclic thiol) to form self-assembly (SA) films, which further reacted with epoxy resin to generate a strong adhesion interface. The structure and composition of untreated and treated CF surface were investigated by surface-enhanced Raman scattering spectroscopy (SERS) and X-ray photoelectron spectroscopy (XPS), respectively. SERS study showed that thiols chemisorbed on Ag-plated CF in the form of thiolate species via the strong S—Ag coordinative bond. Moreover,

adsorbate orientation of thiols SA films on Ag-plated CF surfaces was revealed on the basis of SERS selection rules. The XPS study further confirmed the well organized alignment and the chemisorption of thiols. To understand the interfacial adhesion mechanism, the interfacial shear strength of CF/epoxy microcomposites was evaluated by the microbond technique. The results showed that among the parameters such as chain lengths, molecular orientation, and types of functional groups, the chemical nature of functional groups is most important for the improvement of interfacial properties in CF/epoxy composites. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 3380–3387, 2009

Key words: composites; carbon fiber; interfacial adhesion; Raman spectroscopy and scattering; thiols self-assembly

INTRODUCTION

Interfacial adhesion plays an important role in determining the mechanical properties of composites, especially carbon fiber (CF)/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,[1,2] coating,[3,4] grafting,[5,6] 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 that 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 interchain van der Walls forces. The objective of this study is to introduce such assembly method into interface between CF and epoxy matrix. Although SAMs systems have occupied a wide range of applications in the fields of biology, microelectronics, optics, and coatings,[7–10] it's studies in composite systems have been less frequently reported. Lu et al.[11] 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 strength and higher elongation than

those of the untreated systems. To our knowledge, no studies concerning SA films at CF/epoxy interface have been considered so far.

In this article, three types of thiols are chosen for forming the self-assembly films on Ag-plated CF surfaces: hydroxyl-substituted alkanethiols [HO$(CH_2)_n$SH, C_n in short], amino-substituted aromatic thiol, and organic heterocyclic thiol, respectively. The possibility of changing the chain lengths, molecular orientation, and terminally functional groups makes self-assembly (SA) attractive model system to study the nature of interfacial adhesion of CF/epoxy composites at the molecular scale. Among those parameters that might have a strong effect on the interfacial properties of CF/epoxy composites are anticipated.

EXPERIMENTAL

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 Corp. The fibers used in the article were polyacrylonitrile based carbon fibers, which were 1 K, high strength type, provided by Jilin Carbon Factory, China.

Alkanethiols used in this study were limited to 2-mercaptoethanol (HO$(CH_2)_2$SH, C_2 in short, 99% purity), 6-mercapto-1-hexanol (HO$(CH_2)_6$SH, C_6, 97%), 11-mercapto-1-undecanol (HO$(CH_2)_{11}$SH, C_{11}, 97%). Aromatic thiol was limited to 4-aminothiolphenol (H$_2$N(C$_6$H$_4$)SH, ATP, 96%). Organic heterocyclic thiol was limited to 2-mercaptobenzothiazole (chemical structure shown in Fig. 1, MBT, 96%). 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.

Preparation of thiols SA films on Ag-plated CF

About the technique and morphology of the electroless Ag plating on CF surfaces, please refer to another literature[12] of author. The Ag-plated carbon fibers were separately immersed into 0.5 mM solutions of five thiols in ethanols for $\sim$ 24 h at room temperature. After the modification, the fibers were rinsed thoroughly, first with pure ethanol and then with deionized H$_2$O to clean the surface from residues of the modification solution, then dried with a stream of nitrogen gas.
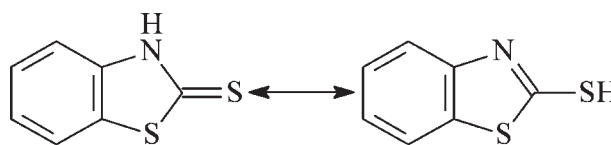

Figure 1 The chemical structure of heterocyclic thiol MBT (a) thione (b) thiol.

SERS measurement of thiols adsorbed onto Ag-plated CF

SERS spectra of SA films on Ag-plated CF 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°.

XPS measurement of thiols SA films on Ag-plated CF

XPS measurements were performed utilizing a thermo ESCALAB 250 photoelectron energy spectrometer. The spectra were collected using a AlKα X-ray source (1486.6 eV). The binding energy scale was calibrated by C1s (284.6 eV). The X-ray power of the photoelectron was set at 200 W, respectively.

Testing of interfacial shear strength of modified CF/epoxy composites

A microbond test was performed to evaluate the interfacial shear strength (IFSS) between CF and matrix by pulling out a fiber from cured epoxy resin droplet. 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 Corp. of Japan.

RESULTS AND DISCUSSION

Alkanethiols self-assembly films on Ag-plated CF surfaces

SERS analysis

Figure 2 shows the normal Raman spectrum (NRS) of C_2 solid and its surface enhanced Raman spectrum (SERS) on the Ag-plated CF substrate, respectively. It is seen that the SERS spectrum is strikingly different from the solid. The strong Raman band of the S—H stretching vibration at 2566 cm^{-1} in curve a disappears in curve b, the missing S—H stretching band indicates the generation of the expected
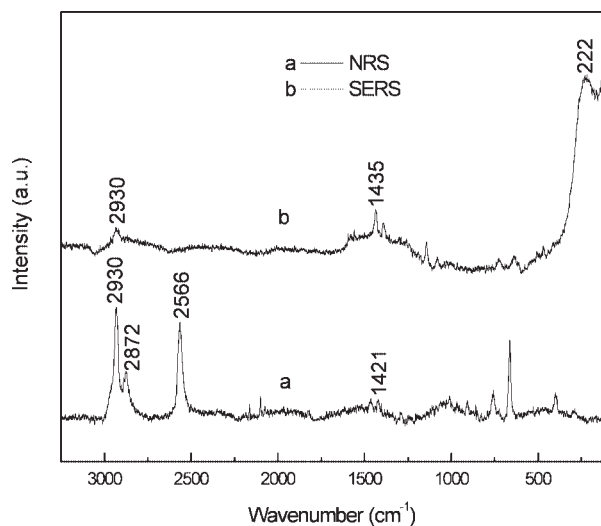
Figure 2 The normal Raman spectroscopy of C_2 and its SERS on Ag-plated CF surfaces.

covalent bonding of the sulfur atoms to the Ag surface, which is demonstrated by the appearance of a new band at 222 cm^{-1} assigned to the Ag—S bond in curve b. That is to say, C_2 species were chemisorbed onto the Ag-plated CF surface by the splitting of the S—H bond to form its thiolate. At the same time, doublet peaks are observed at 2930 and 2872 cm^{-1} in curve a, attributed to the asymmetrical and symmetrical —CH$_2$ stretching vibration modes of C_2. By comparison, the doublet peaks are dramatically attenuated in the intensity in curve b. This means the C—H stretching modes are parallel to the Ag-plated CF substrate according to the SERS selection rules.[13] That is, the methylene chains are aligned almost perpendicularly to the substrate surface. So, it can be concluded that C_2 forms a standing-up phase on the surface. On the contrary, from curve a to b, the weak intensity and narrow peak in the vicinity of 1421 cm^{-1} band assigned to the —CH$_2$ bending vibration mode is dramatically enhanced and broaden. The comparison of the normal Raman spectra and its SERS spectra of C_6 and C_{11} molecules are similar to those of C_2 (not shown here).

XPS analysis

Figure 3 provides the wide-scan XPS spectra of three SA films (C_2, C_6, C_{11}) on Ag-plated CF surfaces at two different photoemission angles, 30° and 90°. The intensity data of Ag, S, and C elements are summarized in Table I.

From Figure 3 and Table I, we can see the following rules relating to the ratios of Ag to C in intensity: (1) For the same film, with the decrease of the emission angle from 90° to 30°, the relative intensity of Ag gradually attenuates and the intensity of C

enhances; (2) For the self-assembly films with various chain lengths, the intensity of C in the longest chain C_{11} molecules has a greater increment than that of C in short chain C_2; (3) At the same photoemission angle, the relative intensity of C is in the order of $C_{11} > C_6 > C_2$. Furthermore, we can also see the following variation rules relating to the ratios of Ag
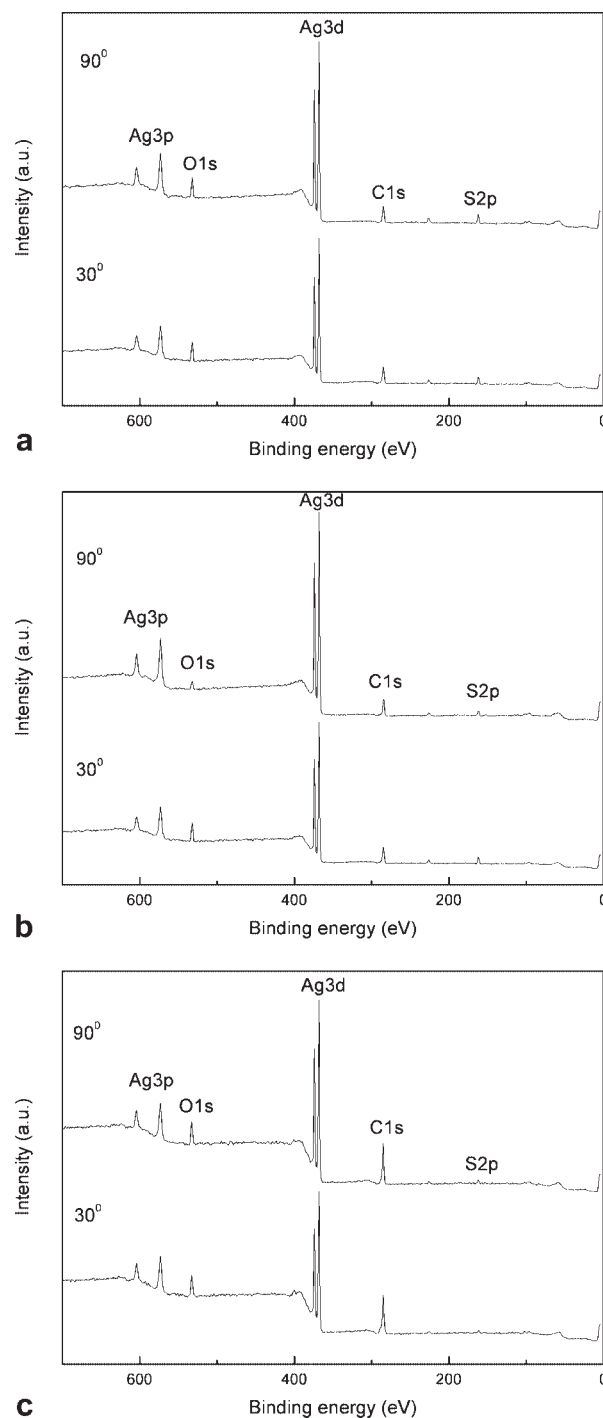

Figure 3 The comparison of XPS spectra of three C_n SA films at two different photoemission angles, 90° and 30° (a) C_2 films (b) C_6 films (c) C_{11} films.

TABLE I
The XPS Intensity of Three C_n Self-Assembly Films

Take off (°)	Self-assembly films	Ag3d	C1s	S2p	Ag : C	Ag : S	C : S
30	C_2	98,371	17,115	6099	1 : 0.17	1 : 0.062	2.806 : 1
	C_6	96,157	18,269	3942	1 : 0.19	1 : 0.041	4.634 : 1
	C_{11}	87,483	32,368	2086	1 : 0.37	1 : 0.024	15.517 : 1
90	C_2	122,627	11,036	6744	1 : 0.09	1 : 0.055	1.636 : 1
	C_6	134,150	14,458	4695	1 : 0.11	1 : 0.035	3.079 : 1
	C_{11}	90,858	28,541	1908	1 : 0.31	1 : 0.021	14.959 : 1

to S in intensity: (1) With the decrease of the emission angle, the relative intensity of S in three films increases slightly; (2) At the same emission angle, the intensity of S in short chain compound is greater than that of S in long chain compound. The above results show that three SA films on Ag-plated CF surface are uniform and the molecular alignment in films is well organized.

Figure 4 presents the comparison of XPS spectra of three SA films at the same photoemission angle 90°. Firstly, from the peak areas of all elements, we could get the accurate amount of self-assembled alkanethiols (C_2:52%; C_6: 59%; C_{11}: 71%). The noteworthy point is that the depth of XPS measurement is less than 10 nm, whereas the coverage thickness of Ag on CF surface is 80 nm or so. Therefore, the elements C, O, S in XPS spectra come from the thiol molecules, not concerned with the CF; Then, from Figure 4 and Table I, we can also see the variation relationship about the ratio of C to S in intensity. At the same photoemission angle, with the increase of alkyl chain length, the intensity of C gradually increase, whereas the intensity of S gradually decrease, which is in accord with the result of S

narrow-scan spectrum in different films, as shown in Figure 5. But the ratios of C to S in Table I are not completely consistent with the atom ratios of C to S in three films (C_2: 2 : 1; C_6: 6 : 1; C_{11}: 11 : 1). This could be explained that self-assembly films exposed to air might be contaminated.

XPS has been widely used to characterize the attachment of the sulfur on the metal substrates.[14,15] Figure 5 also presents the deconvoluted peak of the S 2p spectrum from C_2 SA films on Ag-plated CF surface. The sulfur spectra are fitted by $S2p_{3/2}$ and $S2p_{1/2}$ doublets that are separated by 1.2 eV. In the majority of literatures,[14–16] the unbound thiol molecules have been observed at binding energies between 163 and 165 eV. So, the $S2p_{3/2}$ binding energy of 161.8 eV could be assigned to be "thiolate." This demonstrated the existence of a chemical metal-sulfur bond.

So, through the analysis of Raman and XPS, it could be concluded that alkanethiols SA films are well organized and oriented perpendicularly to the Ag-plated CF surfaces. Also, it could be demonstrated that alkanethiols chemisorb onto CF substrate by the formation of Ag—S bond.
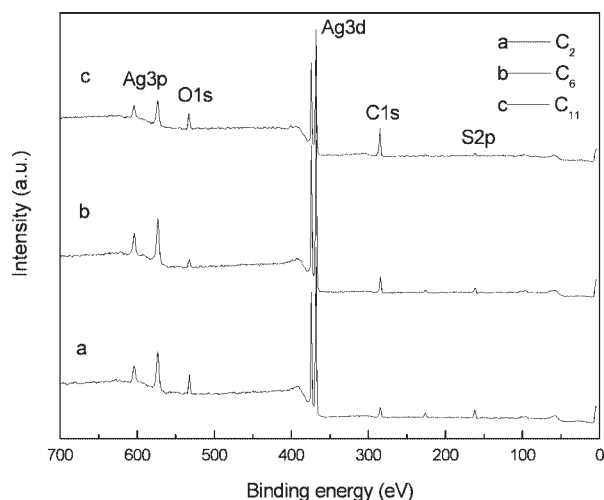

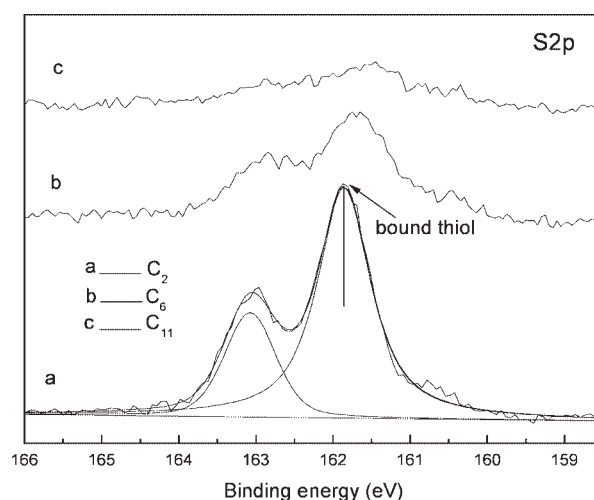**Figure 4** The comparison of XPS spectra of three C_n SA films at 90°.

Figure 5 The comparison of S2p XPS spectra of three C_n SA films at 90°.

Aromatic thiol self-assembly films on Ag-plated CF surfaces

SERS analysis

Figure 6 gives the normal Raman spectrum of ATP and SERS spectrum of ATP film on Ag-plated CF surfaces. A special attention is paid to the latter region from 2500 to 3100 cm^{-1} range in the spectrum. A normal Raman spectrum of ATP shows a peak at 2561 cm^{-1} attributed to the S—H stretching band, whose counterpart is completely absent after adsorption in curve b. This implies ATP adsorbed on the Ag surface after losing its thiol proton. Meanwhile, the appearance of the new Ag—S band at 225 cm^{-1} indicates the chemical interactions between the sulfur atoms and the Ag surface. The 3048 cm^{-1} band in the NRS is attributed to the ring C—H stretching band, whereas the ring C—H stretching mode is almost absent in SERS spectrum. The rather abrupt change in intensity for ring C—H stretching band is understandable from SERS selection rules.[17] If the benzene ring of ATP 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, ATP molecular plane is flat on the Ag/CF substrate. Another noteworthy point is that the in-plane C—C stretching mode of the benzene ring of 4-HTP is identified at 1595 cm^{-1}, we observed substantial difference in intensity of these bands in NRS and SERS. Although it is strong in NRS, the intensity has decreased in
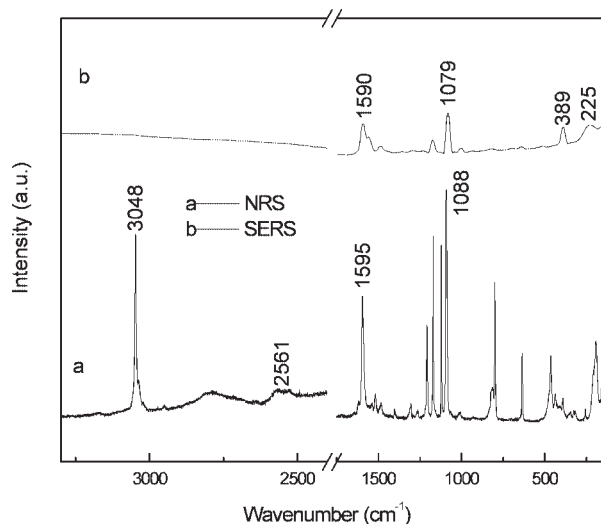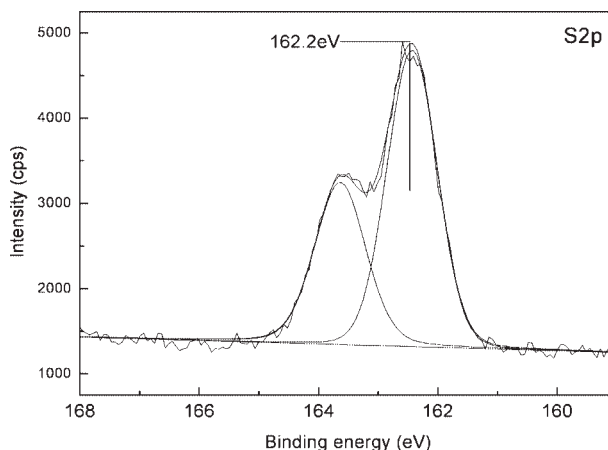
Figure 7 S2p convolution spectrum in ATP aromatic thiol SA films.

SERS. This variation again could be interpreted in terms of SERS selection rules as this mode is along the molecular plane.

XPS analysis

From the peak areas of all elements of XPS (The wide-spectrum not shown here), we could get the accurate amount of 45% of self-assembled ATP aromatic thiol on Ag-plated CF surfaces. Figure 7 presents the deconvoluted peak of the S 2p spectrum from ATP SA films on Ag-plated CF surface. The S 2p spectrum is similar to that in Figure 5. Only the difference lies in the variation of binding energy of S2p$_{3/2}$ from 161.8 to 162.2 eV. The shift change is primarily due to the different chemical environment of S atom. Likewise, the binding energy 162.2 eV is also assumed to be the characteristic of S—Ag bond because the binding energy of unbound sulfur species is always be found to be the range between 163 and 165 eV.

Organic heterocyclic thiol self-assembly films on Ag-plated CF surfaces

SERS analysis

Figure 8 presents the normal Raman spectrum of MBT and SERS spectrum of MBT film on Ag-plated CF surfaces. MBT solid could exist in both thiol and thione forms. 1495, 1251, and 1129 cm^{-1} bands in NRS attributed to the characteristic of thione structure completely vanish in SERS which shows adsorption of MBT onto Ag/CF surface in the thiol form. The striking feature that comes to immediate attention is the substantial changes in the C—H region from 2500 to 3200 cm^{-1}. A normal Raman spectrum (NRS) of MBT shows a weak peak at 2638 cm^{-1} attributed to the S—H stretch. This completely

Figure 6 The normal Raman spectroscopy of ATP and its SERS on Ag-plated CF surfaces.
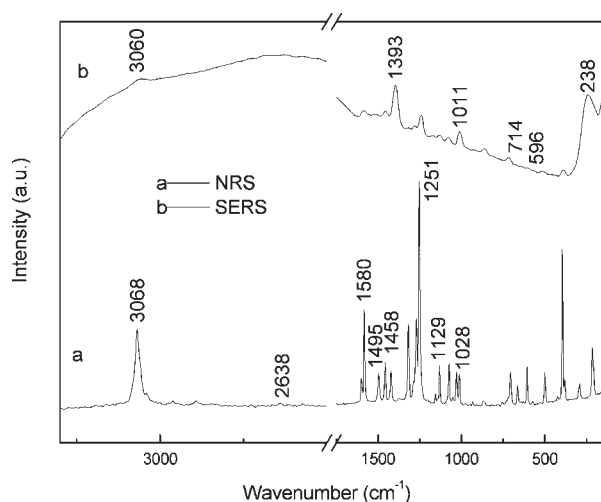
Figure 8 The normal Raman spectroscopy of MBT and its SERS on Ag-plated CF surfaces.

vanishes on adsorption. But a new band occurred at 238 cm^{-1} attributed to Ag—S bond. This could demonstrate the chemisorption of MBT on Ag/CF. In addition, the adsorbate orientation of MBT could be obtained on the basis of SERS selection rules. The 3068 cm^{-1} band in the NRS is attributed to the aromatic C—H stretches, though the intensity of the counterparts in SERS is very weak and the frequency is downshifted by 8 cm^{-1} from 3068 to 3060 cm^{-1}. This implies the alignment of MBT molecules is almost parallel to substrate surfaces with a small tilt angle. Meantime, it could be seen that benzene modes at 1580 and 1011 cm^{-1} also strikingly weaken, but not vanish, further demonstrating the almost lying-down orientation with a small tilt angle.
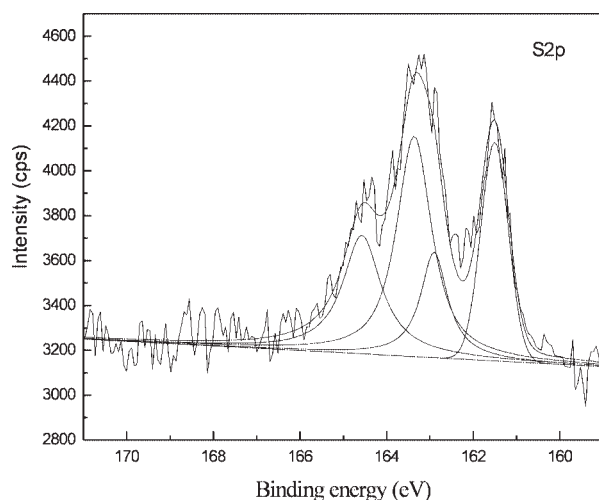

Figure 9 S2p convolution spectrum in MBT heterocyclic thiol SA films.

XPS analysis

From the peak areas of all elements of XPS (The wide-spectrum not shown here), we could get the accurate amount of 49% of self-assembled MBT organic heterocyclic thiol on Ag-plated CF surfaces. Figure 9 also presents the deconvoluted peak of the S 2p spectrum from MBT SA films on Ag-plated CF surface. The difference from C$_2$ and ATP films lies in the two group double peaks, corresponding to S of out-of-heterocycle (161.5, 162.9 eV) and S of in-heterocycle (163.4, 164.6 eV). Likewise, the binding energy at 161.5 eV is the characteristic of S—Ag bond.

In line with the above Raman and XPS spectral studies, it is reasonable to propose that surface functionalized alkanethiols, aromatic thiol, and heterocyclic thiol SA films were chemisorbed onto the Ag/CF substrate through S atoms to form thiolated species. As expected, alkanethiols films with various chain lengths covered the Ag/CF surface with —OH groups at a stand-up alignment. Whereas aromatic thiol ATP and heterocyclic thiol MBT films were adsorbed onto the Ag/CF substrate with a flat orientation and close to flat orientation with a small tilt angle.

Interfacial analysis of CF/epoxy microcomposites

The interfacial shear strength (IFSS) increment of modified CF/epoxy composites compared to untreated composites are shown in Figure 10. The results indicate that self-assembly treatment on CF surface improved the interfacial adhesion 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.
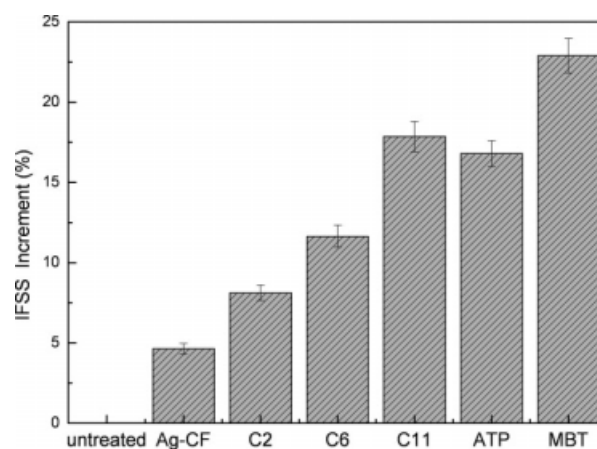

Figure 10 The effect of alkanethiols, aromatic thiol, and heterocyclic thiol SA films on the IFSS of CF/epoxy composites.

Prior to self assembly, IFSS of Ag-plated CF composites is increased by 4.63%. This explanation has been given in the literature.[12]

For hydroxyl substituted alkyl thiols SA films, after Ag/CF surfaces are assembled with C_2, C_6, and C_{11}, respectively, IFSS values of composite samples all increase and are improved by 8.12, 11.64, 17.85% compared to untreated composite. They are chemisorbed onto Ag/CF 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 CF were almost determined by the hydroxyl end-groups on SA film surfaces. By the chemical interaction of the ─OH end-groups and epoxy matrix, strong interfacial adhesion layers generated. Thus, SA films/Ag is able to act as coupling agents between CF and epoxy resin to enhance the interfacial adhesion. Moreover, the longer the alkyl chain, the higher the IFSS value. This may be explained because of the fact that SA films 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 C_2 determines the less-ordered molecular packing with less functional groups exposed on outermost surface, which is the result of low IFSS values.

For aromatic thiol and heterocyclic thiol SA films, after Ag/CF surfaces are assembled with ATP and MBT, IFSS values of composite samples increase and are improved by 16.80 and 22.90%, respectively. Likewise, the significant increase of interfacial adhesion properties could be attributed to a coupling agent function of both thiols films at interphase region. On one hand, they are also chemisorbed onto Ag/CF via S─Ag bond, which has been verified by SERS and XPS analysis; On the other hand, both ATP and MBT compounds have nitrogen-containing functional groups with high reaction activity toward the epoxy groups of epoxy resin and could participate in the crosslinking curing reaction of epoxy matrix system. Comparing the effect of ATP and MBT on the interfacial properties, MBT has higher IFSS increment than ATP. This could be explained from orientation geometry. Through SERS analysis, it could be known that MBT films cover the substrate surfaces with a small tilt angle, whereas ATP films are aligned completely parallel to substrate surfaces. Thus MBT films have higher thiolate coverage on Ag/CF surfaces than ATP films.

Comparing three types of thiols SA films, aromatic thiol and heterocyclic thiol films have higher IFSS increment than alkanethiols with various chain lengths (except C_{11}). From the amount of different thiols and IFSS data, at least we could conclude that although the amount of ATP and MBT thiols is low, they have higher IFSS values than alkanethiols. This is because the nitrogen-containing functional groups in ATP and MBT could react with epoxy resin and play a curing agent role. Whereas for alkanethiols, although there is a large amount of ─OH functional groups, the interaction between ─OH and epoxy resin is weak. So, among the parameters such as chain lengths, molecular orientation and types of functional types, the chemical nature of functional groups is most important for the improvement of interfacial properties in CF/epoxy composites.

CONCLUSIONS

In this investigation, we described a general approach to obtain a controlled interface in CF/epoxy composites via self-assembly technique. We chose alkanethiols with various chain lengths, aromatic thiols and heterocyclic thiols to control the interfacial thickness, molecular orientation, and types of interfacial functional groups.

The results of SERS and XPS analysis revealed these organic-sulfur compounds chemisorbed onto the Ag-plated CF surfaces through the formation of Ag-thiolates. In terms of SERS selection rules, it could be concluded that the alkyl chains of alkanethiols SA films were aligned almost perpendicularly to the Ag/CF surface, whereas the benzene rings of aromatic thiol SA films were parallel to the surface, and molecular planes of heterocyclic thiols SA films were close to the lying-down orientation with a small tilt angle. To understand the interfacial adhesion mechanism, the interfacial shear strength of CF/epoxy microcomposites was evaluated by the microbond technique. From IFSS result, it could be concluded that the chemical nature of the functional groups at interphase region is most important for the improvement of interfacial adhesion properties, when compared with the diffusion action of molecular chains between alkyl chain in SA films and epoxy chains in epoxy resin and oriented geometry.

In conclusion, our investigation showed that self-assembly indeed could be a general approach to modify the interface of CF/epoxy composite with good controls in chain lengths, molecular orientation, and types of functional groups.

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