Effect of Silane-Coupling Agents on Interfacial Properties of CF/PI Composites

J. M. He, Y. D. Huang

Faculty of Science, Department of Applied Chemistry, Polymer Materials and Engineering Division, Harbin Institute of Technology, Harbin 150001, People's Republic of China

ABSTRACT: In this article, to form a structure-controlled interface, carbon fiber (CF) surfaces were first activated by plasma technique and then hydroxylated by $LiAlH_4$ treatment, and then were reacted with a suit of silane-coupling agents terminated with desired functional groups to form thin films, which further reacted with polyimide (PI) resin to generate a strong adhesion interface. The morphology, structure, and composition of CF surfaces before and after treatment were investigated by atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS), respectively. The results of FTIR and XPS analysis showed that silane-coupling agents were successfully chemisorbed onto the CF surfaces by the hydrolysis and condensation reactions. The interfacial shear strength of the CF/PI microcomposites was evaluated by the microbond technique. The results showed that the types of the interfacial functional groups, especially the vinyl end groups in vinyltriethoxysilane (VS), which can react with PI resin, had very significant influence on the improvement of the interfacial adhesion properties of composites. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2231–2237, 2007

Key words: carbon fiber; composites; silane; interface

INTRODUCTION

Interfacial adhesion plays an important role in determining the mechanical properties of composites. Carbon fibers (CFs), without any surface treatment, cause a weak adhesion to the matrix resin. Consequently, a variety of surface treatments of CFs such as oxidation,[1,2] coating,[3,4] grafting,[5,6] and plasma,[7,8] etc., are developed. All surface treatments enhance the interfacial shear strength (IFSS) by introducing chemically active groups on the fiber surfaces, which increase the reactivity with the matrix, enhancing the surface roughness to produce better mechanical interlocking as well as increasing the surface energy for improved wetting. However, how these surface treatments ultimately influence the interfacial properties are not yet fully understood because of the difficulties in quantitatively defining and controlling both the interfacial thickness and surface distribution, types of organic functional groups on CF surfaces. So, there is an urgent need to search for an appropriate method, which can simplify and model various complex interfaces to gain a better insight into the interfacial action mechanisms.

In this article, the hydroxylated surface/silane-coupling agents system was introduced into the interface of CF/PI (polyimide) composite. Although silane-coupling agents have been widely used for surface treatment of glass fiber-reinforcing composites, their studies in CF composites have been less frequently reported because of inert CF surfaces. Hence, the hydroxylation of CF surfaces is prerequisite for the modification of silane-coupling agents. A new treatment method based on hydroxylated surface/silane system on CF surfaces is anticipated to control the types, density, and organized array of interfacial functional groups at the molecular level by selecting silanes with desired end groups.

The method proposed mainly consists of the following steps: (a) hydroxylation of CF surfaces; (b) reaction of silane-coupling agents on hydroxylated CF surfaces; and (c) the generation of the strong adhesion interface layer in modified CF/PI composite. Atomic force microscopy (AFM) was used to observe the morphology of CF surfaces before and after modification. We examined the adsorption behavior of silane thin films on hydroxylated CF surfaces by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The IFSS values of CF/PI microcomposites were obtained using the microbond test.
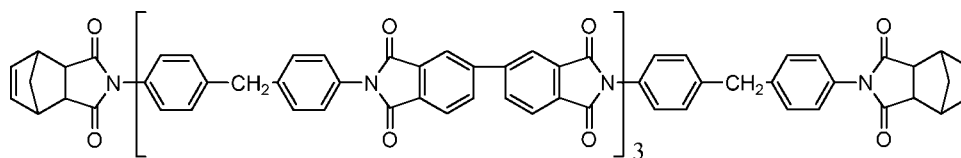
Figure 1 The chemical structure of polyimide (PI) oligomer.

EXPERIMENTAL

Raw materials

The resin used in this study was PI, which was supplied by the Changchun Institute of Applied Chemistry, China. The chemical structure of PI precursor was indicated in Figure 1. The fibers used in this work were polyacrylonitrile-based CFs, which were 1 K, high strength type, provided by the Jilin Carbon Factory, China.

Preparation of silane thin films on CF surfaces

Hydroxylation of CF surfaces

Firstly, the extracted CFs were oxidized using the plasma technique at the power of 40 W for 10 min. Surface-oxidized CFs were immersed in LiAlH$_4$-THF saturated solution, and the mixture was refluxed for 1 h. After reduction treatment, the fibers were washed with a 10% H$_2$SO$_4$ solution for the removal of adsorbed aluminum hydroxide formed during the reduction treatment. Finally, the fibers were washed and hot extracted with doubly distilled water for 48 h and dried.

Treatment of silane-coupling agents on hydroxylated CF surfaces

The following silane-coupling agents were chosen for the preparation of thin films on hydroxylated CF substrates: vinyltriethoxy silane (CH$_2$=CHSi(OC$_2$H$_5$)$_3$, denoted later as VS, 99% purity), methyltrimethoxy silane (CH$_3$Si(OCH$_3$)$_3$, MS, 96%), γ-aminopropyltriethoxy silane (H$_2$N(CH$_2$)$_3$Si(OC$_2$H$_5$)$_3$, APS, 97%), γ-glycidoxypropyltrimethoxy silane (CH$_2$OCHCH$_2$O(CH$_2$)$_3$Si(OCH$_3$)$_3$, GPS, 99%). They were purchased from Aldrich Chemical and used as received without further purification.

The hydroxylated CFs were separately immersed into 1 mM solutions of above-mentioned silanes in ethanols for ∼ 8 h at room temperature. After reaction, the fibers were rinsed many times, first with pure ethanol and then with deionized H$_2$O to clean the surface from residues of the modification solution, dried at 110°C for 10 min, and then cooled in a vacuum desiccator.

XPS analysis of silane-treated CF surfaces

XPS measurements were performed utilizing a Thermo ESCALAB 250 photoelectron energy spectrometer. The spectra were collected using an Al Kα X-ray source (1486.6 eV). To compensate for the surface charging, all the binding energies of the core-level spectra were referenced to the C1s hydrocarbon peak at 284.6 eV. The pass energy for the analyzer was 20 eV with the emission angle of 90° and a power of 200 W.

FTIR analysis of silane-treated CF surfaces

Fourier transform infrared spectra (FTIR) of CF surfaces were obtained with a Nexus670 spectrometer from Nicolet Company with a resolution of 1 cm^{-1}. KBr pellets were employed for the testing specimen.

AFM observation of silane-treated CF surfaces

The morphology of CF surfaces before and after modification was examined using a Solver P47 atomic force microscope made in Russia NT-MDT. All images were obtained in the noncontact mode at room temperature. The scanning scope was 4 × 4 μm^2. The AFM images were displayed with different shades of gray (dark gray indicating lower parts and light gray higher parts of the surface).

Interfacial shear test of CF/PI microcomposites

A microbond test was performed to evaluate the IFSS between CF and matrix by pulling out a fiber from cured PI resin droplet. The composite specimens were prepared by dipping PI resin droplets on CF monofilament with the embedded length of 60–80 μm using a fine-point applicator. The specimens were cured at 120°C for 2 h, then cured at 210°C for 2 h, and finally cured at 316°C for 3 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, Japan. The pull-out test was performed at a crosshead displacement rate of 0.5 μm/s. The value of IFSS was calculated according to the equation
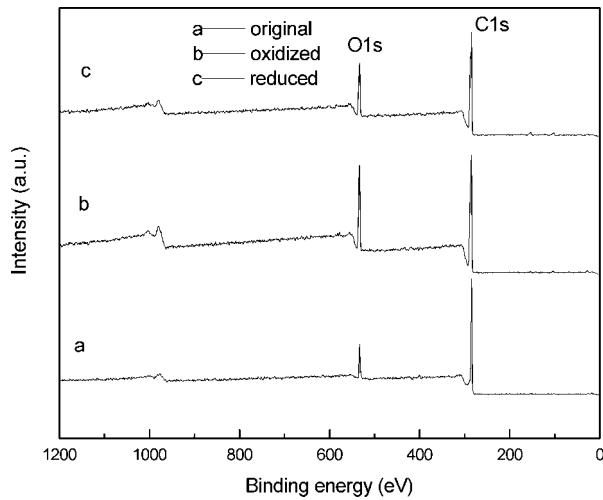
$$\text{IFSS} = \frac{F}{\pi dl}$$

Figure 2 XPS total spectra of CF surfaces.

where F is the maximum load, d is the diameter of the CF, and 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.

RESULTS AND DISCUSSION

Hydroxylation of CF surfaces

After the CFs were oxidized by plasma technique and reduced by LiAlH$_4$ treatment, the changes of their surface element contents were measured by XPS. Figure 2 provides the wide-scan XPS spectra of the original, oxidized, and reduced CFs. The composition and contents of CF surfaces are listed in Table I.

When compared with the untreated CF, the oxygen-containing concentration on oxidized CF surface greatly increases, whereas the carbon-containing concentration significantly decreases, as indicated in Figure 2 and Table I. The results show an increase in the O : C ratio from 0.118 to 0.251. This reveals that the plasma treatment can effectively oxidize the CF surface and introduce more oxygen-containing groups. After the oxidized CF surfaces were reduced by LiAlH$_4$, there is a slight decrease in the O : C ratio from 0.251 to 0.203.

TABLE I
The Composition and Contents of the Elements on CF Surfaces

Samples	Composition and contents of the elements (%)			
	C	O	N	O/C
Original CF	88.74	10.48	0.78	0.118
Oxidized CF	79.42	19.91	0.67	0.251
Reduced CF	82.53	16.76	0.71	0.203

To accurately obtain the contents of the functional groups of CF surfaces, the C1s curve fitting spectra of CF surfaces were presented in Figure 3. After the CF was oxidized, when compared with untreated CF, the contents of the oxygen-containing functional groups such as hydroxyl, carbonyl, and carboxyl
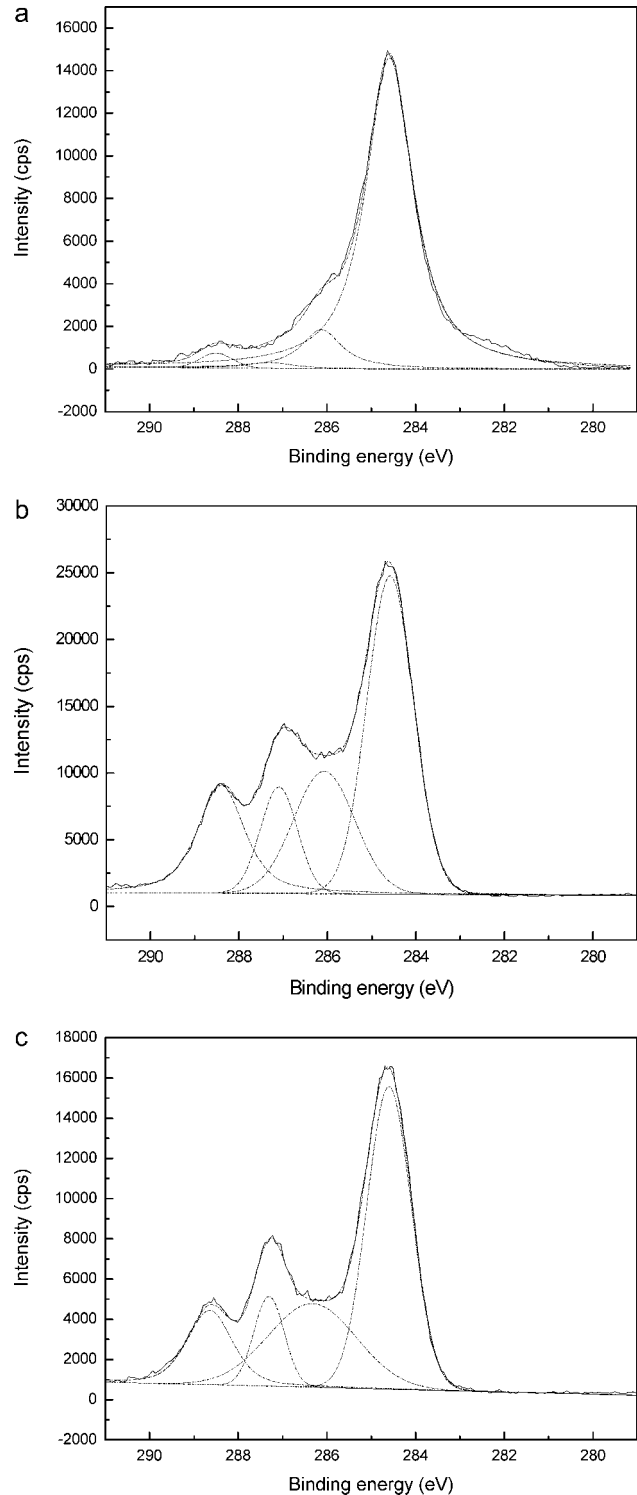

Figure 3 C1s XPS spectra of CF surfaces before and after treatment: (a) original, (b) oxidized, and (c) reduced.

| | Contents of functional groups of CF surfaces | | | | | | | |
| | C—C | | C—OH | | C=O | | COOH | |
Samples	BE (eV)	%	BE (eV)	%	BE (eV)	%	BE (eV)	%
Original CF	284.6	72.7	286.1	14.0	287.3	4.6	288.5	8.8
Oxidized CF	284.6	45.7	286.1	22.9	287.1	12.1	288.4	19.3
Reduced CF	284.6	49.1	286.3	26.9	287.3	9.8	288.6	14.2

increase, especially in carboxyl groups. After reducing reaction, when compared with oxidized CF, the fractions of carbonyl and carboxyl groups obviously decrease, which implies that LiAlH$_4$ as the reduction reaction catalyst is nonselective,[9] whereas the fraction of hydroxyl groups increases from 22.9% to 26.9%, as shown in Table II. That is, small amounts of carboxyl and carbonyl groups are converted to the expected hydroxyl groups. As a whole, although the conversion of carbonyl and carboxyl groups to the hydroxyl is incomplete, hydroxyl fraction on CF surfaces is greatly enhanced from original 14.0% to 26.9%. Therefore, CF surfaces with higher hydroxyl fraction were still hopeful as substrates for the following silane-coupling agents treatment.

Reaction of silane-coupling agents on hydroxylated CF surface

The chemical structure, composition, and topography of a suite of silane-treated CF surfaces were characterized by FTIR, XPS, and AFM, respectively.

FTIR analysis of silane-treated CF surfaces

Figure 4(a–d) shows the FTIR spectra of CF surfaces treated with silanes of VS, MS, APS, and GPS, respectively. In Figure 4(a), the strong peaks at 3433 and 1629 cm^{-1} attribute to the hydroxyl stretching and bending vibration modes, derived from the unreactive hydroxyl, CF surfaces itself, or hydrolyzed silanol groups. Doublet peaks are observed at 2917 and 2856 cm^{-1}, corresponding to asymmetrical and symmetrical —CH$_2$ stretching vibration modes of CF surfaces itself, which are not covered by silane films. Carbonyl band from CF surfaces itself also appears at 1716 cm^{-1}. Above-mentioned peaks all derive from CF surface itself. In addition, it is noted that the characteristic peak at 1673 cm^{-1} assigned to vinyl end group from VS is observed. From Figure 4(b), corresponding to MS-treated CF, it is seen that all peaks belonging to CF surface itself exist. Most importantly, the characteristic peak at 2971 cm^{-1} corresponding to end-groups methyl from MS arises. Similarly, in Figure 4(c), doublet peaks at 3495 and 3442 cm^{-1} reflect the characteristic peaks of APS

assigned to amino end groups. In Figure 4(d), the weak peaks at 1254 and 934 cm^{-1} attribute to the asymmetric and symmetric stretching vibration modes of epoxy end group from GPS, and 827 cm^{-1} is the bending vibration. A special attention is paid to —Si—O—C and —Si—O—Si stretching bands at 1086, 1049 cm^{-1} from every spectrum. The peaks of —Si—O—C indicate the hydrolysis and condensation reactions between silane and CF substrate happen. The appearance of —Si—O—Si peaks demonstrates the formation of the polysilanoxyl chain by condensation reactions between silane molecules. The another noteworthy point is that the strength of the characteristic peaks of all silane SA films are weak, resulting from two possible factors: on the one hand, the KBr pellet method employed during FTIR testing process reflects the higher strength of bulk CF; on the other hand, the coverage of silane films is poor due to low hydroxyl concentration on CF surfaces.

From the above-mentioned analysis, it can be primarily concluded that the silane films first chemisorbed onto CF surfaces by the hydrolysis and condensation reactions, then formed the polysilanoxyl
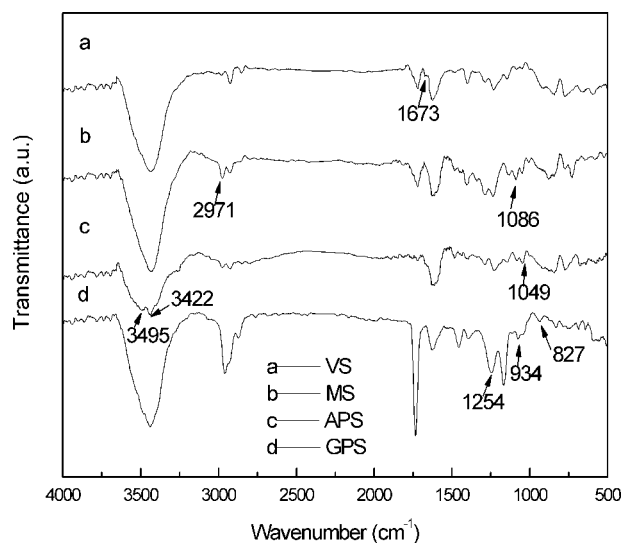

Figure 4 FTIR spectra of silane-treated CF surfaces.

TABLE III
**The Composition and Contents of Silane-Treated
CF Surfaces**

Silane	Composition and contents of the elements (%)			
	C	O	Si	N
VS	81.43	16.86	1.71	—
MS	82.61	15.76	1.63	—
APS	81.95	15.41	1.52	1.12
GPS	79.32	18.62	2.06	—

chains by condensation reactions between silane molecules.

XPS analysis of silane-treated CF surfaces

After silane treatment, the elements and composition of CF surfaces that were performed using XPS measurement were listed in Table III. Si peak is detected in the vicinity of 102 eV in every spectrum (not shown), which reveals that silanes actually adsorbed on CF surfaces. As can be observed from Table III, Si contents are low, which could be explained due to lower concentration of silane solutions and thinner coverage of silane close to monolayers in thickness.

Figure 5 presents the Si 2p curve-fitting spectra from four silane thin films. Possible structures for hydrolyzed silane on CF are shown in Figure 6. In the case of VS-treated CF [Fig. 5(a)], Si 2p spectrum is disassembled into double peaks: lower binding energy at 101.63 eV attributed to —Si(OH)$_3$ structure [Fig. 6(a)], which indicates that the hydrolysis reaction of the ethoxy groups happened and hydrogen bond formed; higher binding energy at 102.50 eV assigned to —SiO$_2$(OH) structure [Fig. 6(c)], which indicates that the condensation reactions occurred. In addition, there is no unhydrolyzed —Si(OC$_2$H$_5$)$_3$ in films since peak of binding energy less than 101 eV does not appear,[10] which reveals that the ethoxy groups containing in VS had completely hydrolyzed. For MS-treated CF, doublet peaks at 102.70 and 102.0 eV attribute to —SiO$_2$(OH) and —SiO(OH)$_2$ [Fig. 6(b)], which indicates the formation of polysilanoxyl chains with short length. The Si 2p analysis of APS-treated CF is similar to that of VS. For GPS-treated CF, only single peak was presented at 102.10 eV assigned to —SiO(OH)$_2$.
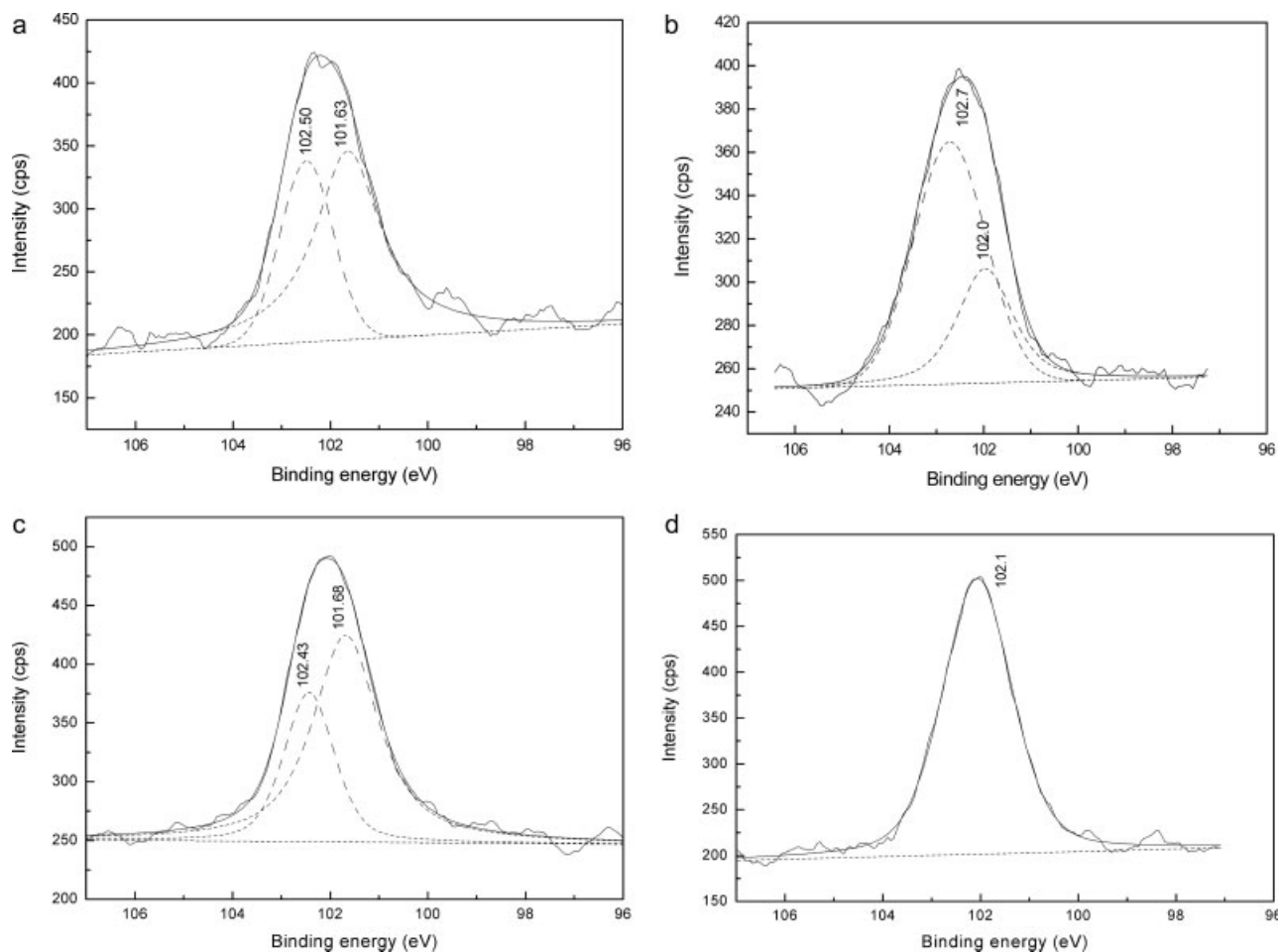

Figure 5 Deconvoluted XPS Si 2p spectra from silane-treated CF surfaces: (a) VS, (b) MS, (c) APS, and (d) GPS.
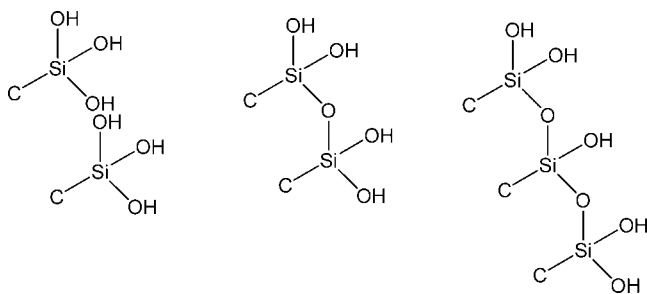
Figure 6 Hydrolyzed and condensed structures of silane-coupling agents on CF surfaces.
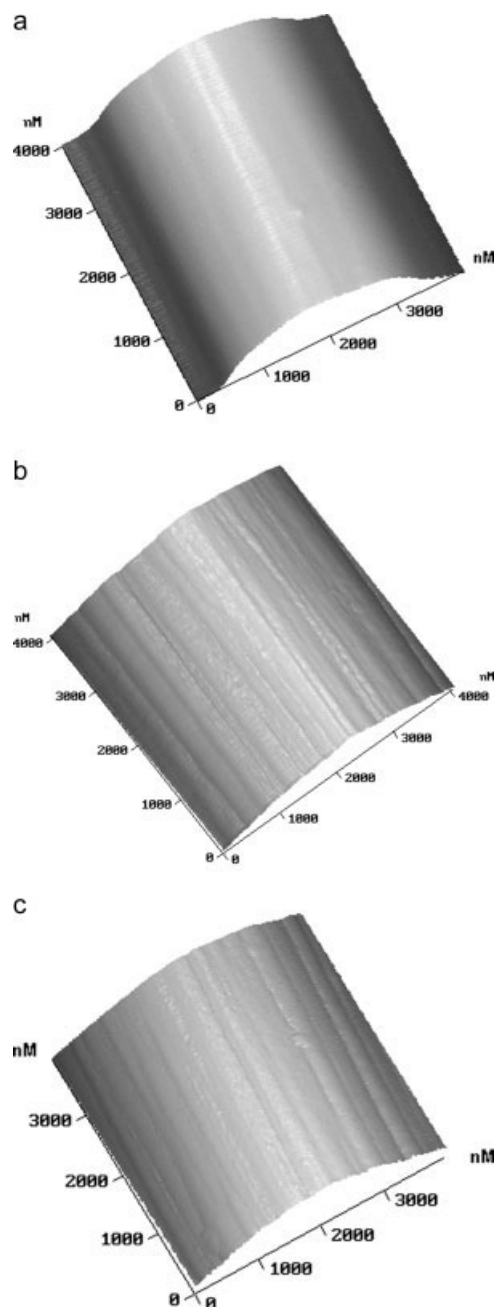

Figure 7 AFM images of CF surfaces: (a) untreated CF, (b) plasma-treated CF, and (c) silane-treated CF.

From the earlier discussion, it could be demonstrated that hydrolysis for every silane on CF surfaces happened and only the condensing extent was different, thus resulting in polysilanoxyl chains with different length.

AFM observation of silane-treated CF surfaces

Figure 7 presents the AFM images of untreated and treated CF surfaces. 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 Figure 7(a). After plasma-treatment [shown in Fig. 7(b)], CF monofilament surfaces take on dense and deeper strip grooves, which indicates that the plasma technique plays double functions on CF surfaces for both oxidization and etching (since AFM image of reduced CF is similar to that of plasma treatment, here not shown). After silane treatment in the case of VS [shown in Fig. 7(c)], it is observed that the CF monofilament surfaces are smooth and uniformly covered by a thin film. Although the concentration of hydroxyl groups of CF surfaces only occupies 26.9%, it is understandable that the silane thin films are almost continuous because of the condensation reactions causing the longer polysilanoxyl chain. Only minority of particles, which are considered to be the self-polymerization species of silane are seen.

From the above-mentioned analysis of FTIR, XPS, and AFM, it could be concluded that the thin films of four silane derivatives with different end groups successfully formed on CF surfaces. A schematic of the silane adsorption mechanism is shown in Figure 8: first, $-Si(OR)_3$ groups hydrolyze to produce
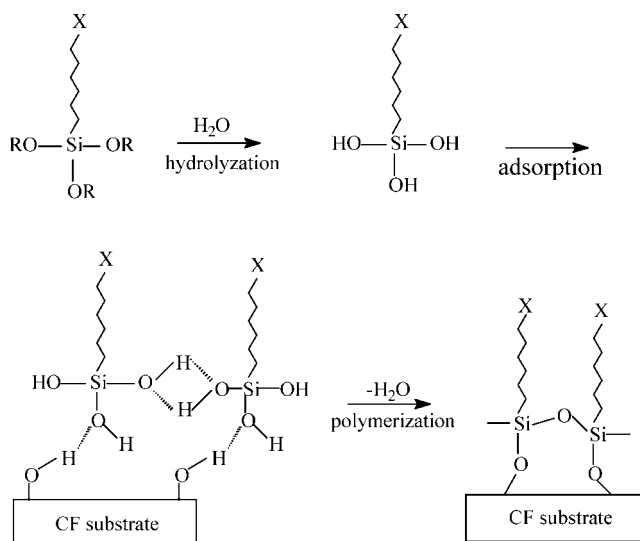

Figure 8 Schematic diagram of the formation of silane thin films on hydroxylated CF surfaces.
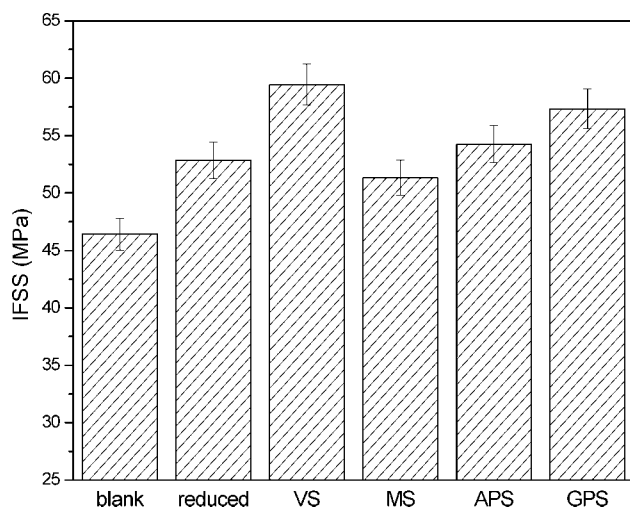
Figure 9 The interfacial shear strength of CF/PI microcomposites.

—Si(OH)$_3$ groups, and then silane molecules accumulated together by van der Waals interaction between alkyl chains to form two-dimensional polymer via Si—O—Si linkage. Meanwhile, dimers combine with surface hydroxylated CF substrate via Si—O—C bond. Finally, dimers began to grow up, consequently forming stable thin films. Therefore, surface properties of CF were controlled by various end groups in the silane thin films.

Interfacial analysis of CF/PI microcomposites

Figure 9 provides IFSS results of PI microcomposites reinforced with untreated and treated CF. From Figure 9, it can be clearly seen that silane thin films on CF surfaces improve the interfacial adhesion force of composites.

Comparing to untreated CF, IFSS of reduced CF composites is improved from 46.43 to 52.86 MPa. It is well-known that increased surface roughness and increased oxygen-containing functional groups on CF surfaces can greatly improve the interfacial adhesion strength of composites.

For four silane thin films when compared with reduced CF, VS with end-group vinyl has largest improvement in IFSS from 52.86 to 59.44 MPa. During PI-curing process, heat is capable of initiating vinyl to produce radical groups, which are liable to crosslink with norbornene-endcapped groups of PI. For this reason, the formation of the majority of the chemical bonds at interface could be mainly responsible for the improvement of IFSS.

GPS terminated with epoxy group has better improvement in IFSS. This may be because epoxy group has good adhesion performance to resin, enhancing the compatibility between CF and PI.

The cause of slight IFSS improvement for APS with end-group amino may be due to the shortage of dissociative acid anhydride in PI oligomers. Consequently, the expected chemical reactions will not occur between silane and PI resin, leading to the lower improvement of interfacial adhesion property.

Different from earlier three silanes, MS with end-group methyl had a slight decrease in IFSS from 52.86 to 51.32 MPa when compared with the reduced CF. This result could be explained that methyl as nonpolar group reduces the activity of CF surfaces, but IFSS is still higher than that of untreated CF/PI composites.

Here, we only discussed the effect of types of functional groups on the interfacial properties at the same concentration of silane solutions. In fact, it would be anticipated that the concentration of silane solutions should have an influence on the thickness of films. Relating to the effect of the interfacial thickness on the interfacial properties is under investigation.

CONCLUSIONS

In this article, the hydroxylated surface/silane-coupling agents system was introduced into the interface of CF/PI composite. To conclude, our investigation demonstrated that the silane-coupling agents were successfully chemisorbed onto CF surfaces to form thin films. By microbond measurement, we found that types of the interfacial functional groups had a very significant influence on the improvement of the interfacial adhesion properties of CF/PI composites, especially the vinyl functional group with reaction to resin.

References

1. Rashkovan, I. A.; Korabelnikov, Y. G. Compos Sci Technol 1997, 57, 1017.
2. Dilsiz, N.; Ebert, E.; Weisweiler, W.; Akovali, G. J Colloid Interf Sci 1995, 170, 241.
3. Yue, Z. R.; Jiang, W.; Wang, L.; Gardner, S. D.; Pittman, C. U. Carbon 1999, 37, 1785.
4. Pamula, E.; Rouxhet, P. G. Carbon 2003, 41, 1905.
5. Fieldly, A.; Olsen, T.; Rysjedal, J. H.; Berg, J. E. Compos A 2001, 32, 373.
6. Varelidis, P. C.; Mccullough, R. L.; Papaspyrides, C. D. Compos Sci Technol 1999, 59, 1813.
7. Paredes, J. I.; Martinez-Alonso, A.; Tascon, J. M. D. J Colloid Interf Sci 2003, 258, 276.
8. Bismarck, A.; Kumru, M. E.; Springer, J. J Colloid Interf Sci 1999, 210, 60.
9. Zielke, U.; Huttinger, K. J.; Hoffman, W. P. Carbon 1996, 34, 999.
10. Wang, Y. H.; Yu, Q.; Zhang, Y. Appl Surf Sci 2004, 229, 377.