

# Formation of a carbon fiber/polyhedral oligomeric silsesquioxane/carbon nanotube hybrid reinforcement and its effect on the interfacial properties of carbon fiber/epoxy composites

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ARTICLE INFO

Article history: Received 9 August 2010 Accepted 13 February 2011 Available online 17 February 2011

# ABSTRACT

A carbon fiber/polyhedral oligomeric silsesquioxane/carbon nanotube (CF-POSS-CNT) hybrid reinforcement was prepared by grafting CNTs onto the carbon fiber surface using octaglycidyldimethylsilyl POSS as the linkage in an attempt to improve the interfacial properties between carbon fibers and an epoxy matrix. X-ray photoelectron spectroscopy, scanning electron microscopy, dynamic contact angle analysis and single fiber tensile testing were performed to characterize the hybrid reinforcements. Interlaminar shear strength (ILSS), impact toughness, dynamic mechanical analysis and force modulation atomic force microscopy were carried out to investigate the interfacial properties of the composites. Experimental results show that POSS and CNTs are grafted uniformly on the fiber surface and significantly increase the fiber surface roughness. The polar functional groups and surface energy of carbon fibers are obviously increased after the modification. Single fiber tensile testing results demonstrate that the functionalization does not lead to any discernable decrease in the fiber tensile strength. Mechanical property test results indicate the ILSS and impact toughness are enhanced. The storage modulus and service temperature increase by 11 GPa and 17 °C, respectively. POSS and CNTs effectively enhance the interfacial adhesion of the composites by improving resin wettability, increasing chemical bonding and mechanical interlocking.

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# 1. Introduction

It is widely accepted that the mechanical properties of carbon fiber composites are highly dependent on the interphase between fibers and matrix [1,2]. An appropriately engineered interphase can significantly improve the strength, toughness and environmental stability of the composites and transfer the stress efficiently from matrix to carbon fibers [3]. However, smooth and chemically inert fiber surfaces usually result in poor matrix compatibility and weak adhesion

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between fibers and matrix [4]. As a result, extensive research has been devoted to the surface treatment of carbon fibers in order to improve their interfacial adhesion, such as oxidation treatment, electrochemical method, plasma treatment and high energy irradiation, by introducing reactive groups onto the fiber surface, changing the surface energy to increase the wettability, or increasing the fiber surface roughness to enhance mechanical interlocking [5–8].

The excellent mechanical properties of CNTs make them ideal nanofillers in composite fields. Recently, grafting CNTs onto the carbon fibers or growing CNTs through chemical vapor deposition directly onto the fiber surface have attracted considerable technical and commercial interest due to their use for CNT based hierarchical composites [9,10], because CNTs could offer both intralaminar and interlaminar reinforcement, and improve delamination resistance and through-thickness properties without compromising in-plane performance [11]. Although grafting CNTs onto fiber surfaces is an effective method to increase fiber surface area, create mechanical interlocking, or locally stiffen at the interface, all of which may improve stress transfer and interfacial properties, the lack of chemical bonding limits the further increase of the interfacial properties of the resulting composites. Moreover, the decreased carbon fiber surface energy caused by the more hydrophobic CNTs grafted on the carbon fiber surface usually lead to poor wettability by viscous matrices [12].

The huge interest in polyhedral oligomeric silsesquioxane (POSS) has been stimulated by their extraordinary intrinsic properties, at least for unique structures, and wide range of potential applications [13–15]. One of the largest opportunities lies in the area of composite materials. Every POSS molecule possesses eight organic groups which provide POSS molecules with high reactivity and compatibility, which make them attractive for enhancing a variety of matrices. A large number of reports of enhanced strength and modulus, impact resistance, increased thermal and chemical stability, have been observed when POSS is added to a polymer to form a composite [16–18]. Moreover, the organic groups of POSS which can act as a platform for further reaction make POSS a versatile nanoparticle [19]. In a previous study, our group has used POSS to functionalize the carbon fiber surface and



Fig. 1 - Structure of octaglycidyldimethylsilyl POSS.

demonstrated the grafting of POSS molecules could effectively increase the interfacial adhesion and the impact resistance of the resulting composites [20,21].

In this study, we further functionalized POSS grafted carbon fibers through grafting amine functionalized CNTs to the glycidyldimethylsilyl groups on the side chains of POSS in order to study the effect of this newly introduced enhancement component on the interfacial adhesion of the composites. Firstly, this hybrid reinforcement is designed to improve the interfacial adhesion of the resulting composites by using the numerous epoxy groups of POSS to increase fiber surface wettability by the epoxy resin and react with the hardener to enhance chemical bonding. Secondly, the CNTs grafted on the fiber surface, which stick into the matrix, could increase the surface area, enhance mechanical interlocking, and locally stiffen at the interface, which is expected to further increase the interfacial strength. In addition, another aim of this grafting route is to demonstrate that the POSS grafted on the fiber surface can be further tailored to make it more compatible with the matrix or can be used as a scaffold to be functionalized with other reactive molecules if used as functional materials. This novel binary grafting technology could extend the use of carbon fiber in the traditional composite fields, such as commercial aircraft and autos, to produce stronger, tougher and more heat-resistent materials, which would advance the lifespan and safety of these structures. This paper mainly focuses on: (1) effect of POSS and CNTs on the surface characteristics of the carbon fibers and (2) effect of the two enhancement components on the interfacial properties of the resulting composites. The surface chemical composition and morphologies of carbon fibers were characterized by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM), respectively. The wettability of carbon fiber surface was studied by dynamic contact angle analysis. The effect of grafting on the fiber tensile strength was evaluated using single fiber tensile testing. Mechanical properties of the composites were investigated by interlaminar shear strength (ILSS), impact toughness, dynamic mechanical analysis (DMA) testing and force modulation atomic force microscopy (FM-AFM). The structure of octaglycidyldimethylsilyl POSS is shown in Fig. 1. The formation procedure of hybrid reinforcement is illustrated in Fig. 2.



Fig. 2 - Schematic of the formation of CF-POSS-CNT.

# 2. Experimental

# 2.1. Materials

All chemicals were used as received unless stated otherwise. Carbon fibers used in the research were T700SC-12000-50C (12 K, tensile strength 4.9 GPa, diameter 7  $\mu$ m, density 1.8 g cm<sup>-3</sup>), which were purchased from Toray Industries, Inc. The multi-walled CNTs (purity >95%, diameter 10–30 nm, length 1–2  $\mu$ m) were obtained from Shenzhen Nanotech Port Co., Ltd. Octaglycidyldimethylsilyl POSS was purchased from Hybrid Plastics. Thionyl chloride (SOCl<sub>2</sub>), ethylenediamine (EDA), dimethylformamide (DMF) and tetrahydrofuran (THF) were purchased from Sigma–Aldrich. WSR618 epoxy resin (molecular weight 350–400, molecule structure is shown in Fig. 3) and methyl tetrahyelrophthalic anhydride hardener were supplied by Sinopharm Chemical Reagent Co., Ltd., used at a resin to hardener weight ratio of 100:70.

#### 2.2. Experimental procedure

The CF-POSS-CNT hybrid reinforcement was prepared through several steps of chemical reactions. The CNTs were functionalized with EDA using the method similar to the procedure described in the literature [22]. Carbon fibers were refluxed in acetone for 12 h to remove the polymer sizing and pollutants. Then the carbon fibers were oxidized in a 3:1 (v/ v) mixture of concentrated H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> at 60 °C for 2 h. The carboxyl functionalized carbon fibers (CF-COOH) were taken out and washed several times with deionized water until the pH of the wash water was neutral and then dried under vacuum. The CF-COOH was reacted with the mixture solution of 50 ml SOCl<sub>2</sub> and 5 ml DMF at 76  $^\circ\text{C}$  for 24 h, and then the residual SOCl<sub>2</sub> was removed by the reduced pressure distillation to yield acyl chloride functionalized carbon fibers (CF-COCl). Then the CF-COCl was reacted with 50 ml EDA at 80 °C for 24 h to produce amine functionalized carbon fibers (CF-NH<sub>2</sub>). After being washed with deionized water and dried, the CF-NH<sub>2</sub> was mixed with 0.5 g POSS in 100 ml THF reacting at 50 °C for 3 h to obtain POSS grafted carbon fibers (CF-POSS). The CF-POSS was rinsed in excess THF to remove the unreacted POSS and then was mixed with EDA functionalized CNTs in THF under sonication for 20 min to create a homogeneous dispersion, and then reacted at 50 °C for 24 h, during which a 5 min pulsed sonication was implemented on the mixture at 0.5 h intervals. Finally, the prepared CF-POSS-CNT hybrid reinforcement was washed in excess THF under sonication to remove unreacted CNTs. All reactions were carried out under a nitrogen atmosphere.

#### 2.3. Characterization of carbon fibers

The morphologies of the carbon fibers were observed by SEM (S-4800, Hitachi Instrument, Inc. Japan) without gold plating.

The surface roughness of carbon fibers was examined by AFM (Solver-P47H, NT-MDT, Russia) using tapping mode. Each datum was obtained from the average value of 15 different positions on three different fibers.

XPS (ESCALAB 220i-XL, VG, UK) was carried out to study grafting reaction procedure using a monochromated Al K $\alpha$  source (1486.6 eV) at a base pressure of  $2 \times 10^{-9}$  mbar. The XPS was energy referenced to the C1s peak of graphite at 284.6 eV. The XPSPeak version 4.1 program was used for data analysis.

Dynamic contact angle tests were measured by using a dynamic contact angle meter and tensiometer (DCAT21, Data-Physics Instruments, Germany). Deionised water ( $\gamma^{d} = 21.8 \text{ mN m}^{-1}$ ,  $\gamma = 72.8 \text{ mN m}^{-1}$ ) and diiodomethane ( $\gamma^{d} = 50.8 \text{ mN m}^{-1}$ ,  $\gamma = 50.8 \text{ mN m}^{-1}$ , 99% purity, Alfa Aesar, USA) were used as test liquids. Each measurement was repeated three times and the results were averaged.

Single fiber tensile tests were performed on a universal testing machine (5569, Instron, USA) according to the ASTM D3379-75. The results were analyzed with Wellbull statistical method.

#### 2.4. Mechanical property tests of composites

The unidirectional prepreg of carbon fibers and epoxy resin was put into a mold to manufacture composites. The resin content of the composites was controlled at  $35 \pm 1.5$  mass%. The curing process was at 90 °C for 2 h under 5 MPa, 120 °C for 2 h under 10 MPa and 150 °C for 4 h under 10 MPa.

ILSS of the composites was measured on a universal testing machine (5569, Instron, USA) using a three point shortbeam bending test method according to ASTM D2344. Specimen dimensions were 20 mm  $\times$  6 mm  $\times$  2 mm. The specimens were tested at a crosshead movement rate of 2 mm min<sup>-1</sup>, with a span to thickness ratio of 5:1. The recorded value of ILSS for each group of specimens was averaged from the data of 8 successful measurements.

Non-standard impact specimens of 55 mm  $\times$  6 mm  $\times$  2 mm were tested on a drop weight impact test system (9250HV, Instron, USA). The specimens were unnotched. The impact span is 40 mm. The drop weight was 3 kg and the velocity was 1 m s<sup>-1</sup>. Each datum was obtained from the average value of five specimens.

DMA tests were carried out on a dynamic mechanical thermal analyzer (EXSTAR6000 DMS, SII NanoTechnology Inc., Japan) operating in the three-point bending mode at a frequency of 1.0 Hz. Specimen dimensions were 40 mm  $\times$ 6 mm  $\times$  2 mm. The temperature range was 25–200 °C with a heating rate of 2.5 °C min<sup>-1</sup>.

The local modulus of interphase region was investigated on an AFM (Solver-P47H, NT-MDT, Russia) in force modulation mode. A silicon nitride probe with a spring constant of 1–  $5 \text{ N m}^{-1}$  and a resonant frequency of 70–150 kHz was selected. For interface characterization, the composite specimens were



Fig. 3 - Molecule structure of WSR618 epoxy resin.

polished perpendicularly to the fiber axis using increasingly finer sand papers and finally polished with a  $Cr_2O_3$  suspension of an average grain size of 50 nm, and cleaned with water in ultrasonic washer and dried.

# 3. Results and discussion

# 3.1. Surface topography of carbon fibers

The SEM images of untreated carbon fiber, CF–COOH, CF–COCl, CF–NH<sub>2</sub>, CF–POSS and CF–POSS–CNT are shown in Fig. 4a–f, respectively. Remarkable differences of the surface topography can be observed between the untreated and modified carbon fibers. As shown in Fig. 4a, the untreated carbon fiber seems to be relatively neat and smooth, and a few narrow grooves parallel distribute along the

longitudinal direction of the fiber. After the moderate acid treatment, some grooves on the fiber surface become wider and deeper slightly (Fig. 4b), which could be interpreted by acid oxidation and etching. After being reacted with SOCl<sub>2</sub> and EDA, the fiber surfaces become rougher (Fig. 4c and d). As shown in Fig. 4e, on the surface of CF-POSS, a layer of POSS particles appear and the carbon fiber becomes much rougher. The surface roughness increased from 28 nm for the untreated carbon fibers to 76 nm for the POSS grafted fibers. The surface morphology of CF-POSS-CNT is shown in Fig. 4f. The CNTs are covalently grafted and distribute uniformly on the fiber surface at different angles, which makes the carbon fiber look like a branched fiber. Moreover, the fiber surface roughness also further increased to 92 nm. These CNTs sticking into the composite interface region could significantly increase the interfacial adhesion



Fig. 4 – SEM images of (a) untreated carbon fiber, (b) CF–COOH, (c) CF–COCl, (d) CF–NH<sub>2</sub>, (e) CF–POSS and (f) CF–POSS–CNT hybrid reinforcement.

by increasing fiber surface area and enhancing mechanical interlocking between the fiber and the matrix.

# 3.2. XPS analysis

XPS was performed to determine the chemical composition of the carbon fiber surface and carry out a quantitative analysis. The peaks for carbon, oxygen, nitrogen, chloride and silicon are centered at around 284.6, 532.2, 399.5, 201.4 and 103.4 eV, respectively [23-25]. The results of the carbon fiber surface composition are given in Table 1. It is found that the elements of the untreated carbon fiber surface include carbon, oxygen and insignificant amount of nitrogen. Usually, there is only a small amount of oxygen on the untreated carbon fiber surface [23]. However, it should be noted that 14.48% oxygen was detected on the untreated fibers, although they had been refluxed in acetone for 12 h. The C1s curve fit spectrum shows that the fiber surface consists of 68.8% C-C, 25.5% C-O, 3.5% O-C=O and 2.2%  $\pi$ - $\pi$ <sup>\*</sup> transition. The high C–O content may be due to the epoxy groups in the residual epoxy sizing which can be removed by the acid oxidation in the next reaction step and the hydroxyl groups introduced by the electrochemical oxidation in the manufacture process. After moderate acid treatment, the carbon content decreased and the oxygen content increased sharply. From the C1s fit spectrum we can find that the acid treated carbon fiber surface was composed of 61.8% C–C, 17.5% C–O, 18.3% O–C=O and 2.4%  $\pi$ - $\pi$ \* transition. The hydroxyl content decreased and the content of the carboxyl groups which can react with SOCl<sub>2</sub> increased. Although more carboxyl groups on the fiber surface are beneficial to the subsequent grafting reactions, excessive oxidation would seriously decrease the fiber tensile strength. So, the oxidation time and temperature were strictly controlled in order to obtain an appropriate content of carboxyl groups. After the acylation reaction with SOCl<sub>2</sub>, the carboxyl groups on the carbon fiber surfaces were converted to the acyl chloride groups. A noticeable presence of Cl element with a concentration of 4.08% was detected. In the next step of the reactions, the acyl chloride groups were reacted with amine groups of EDA. The significant increase of the nitrogen content suggests the location of amine

Table 1 – Surface element analysis of carbon fibers.								
Samples	C (%)	O (%)	N (%)	Cl (%)	Si (%)			
Untreated CF	84.77	14.48	0.75	-	-			
CF-COOH	70.48	26.46	3.06	-	-			
CF–COCl	71.83	21.68	2.41	4.08	-			
CF-NH <sub>2</sub>	76.75	13.13	9.86	0.24	-			
CF-POSS	63.49	24.17	2.03	0.22	10.08			
CF-POSS-CNT	67.80	23.29	2.37	0.17	6.36			

groups on the carbon fiber surfaces. After POSS was grafted, significant silicon element of 10.08% was obtained on the fiber surfaces. In addition, the C1s curve fit spectrum shows that the POSS grafted fiber surface consisted of 51.3% C-C, 42.6% C-O, 5.3% O–C=O and 0.8%  $\pi$ – $\pi$ <sup>\*</sup> transition. The increased C–O content is due to the epoxy side groups of the octaglycidyldimethylsilyl POSS which can be further reacted with aminefunctionalized CNTs and the hardener in the matrix. At the last step of the reactions, amine functionalized CNTs were grafted on the side chains of the glycidyldimethylsilyl POSS. Silicon content decreased and nitrogen content increased slightly, which was due to the partial envelop of POSS by the grafted CNTs and their amine functionalized end caps. The sufficient epoxy groups on the fiber surface could effectively increase the wettability by the epoxy matrix and enhance the interfacial strength of the composites.

#### 3.3. Dynamic contact angle analysis

The changes of chemical environment and topography of carbon fiber surfaces affect the fiber surface energy as well as its components. The increase of the fiber surface energy could lead to better wettability between carbon fibers and matrix, and improvement of the interface adhesion [26]. In Table 2, the advancing contact angle ( $\theta$ ), the surface energy ( $\gamma$ ), its dispersion component ( $\gamma^{d}$ ) and polar component ( $\gamma^{p}$ ) of the untreated CF and CF-POSS-CNT are summarized. As shown in Table 2, the surface energy of the untreated fibers was 42.01 mN  $m^{-1}\text{,}$  with a dispersion component of 31.73 mN  $m^{-1}$ and a polar component of 10.28 mN m<sup>-1</sup>. After functionalization, obvious decreasing trends of contact angles were observed from the untreated carbon fibers to the modified fibers for both the polar water and the non-polar diiodomethane. The contact angles decreased from  $69.42^{\circ}$  to  $50.18^{\circ}$  for water and from 54.5° to 39.73° for diiodomethane. In addition, the surface energy, its dispersion and polar components of CF-POSS-CNT also obviously increased compared with those of the untreated carbon fibers. In previous studies, we have found that the hybrid reinforcements had more polar and rougher surfaces. The increased polar component of the functionalized fibers was due to the epoxy groups of POSS and the amine groups on the CNT end caps. In addition, the increased dispersion component was due to the increased roughness caused by POSS and CNTs grafted on the carbon fiber surfaces and the differences of graphite structure between carbon fibers and CNTs [27].

# 3.4. Single fiber tensile testing

Single fiber tensile tests were carried out to examine the effect of the modification on the tensile strength of the fibers, which dictates the in-plane properties of the resulting

Table 2 – Contact angles and surface energy of carbon fibers.								
Samples	$\theta_{\text{water}}$ (°)	$ heta_{ ext{diiodomethane}}$ (°)	$\gamma^{d}$ (mN m <sup>-1</sup> )	$\gamma^{p}$ (mN m <sup>-1</sup> )	$\gamma$ (mN m <sup>-1</sup> )			
Untreated CF CF–POSS–CNT	69.42 50.18	54.50 39.73	31.73 39.75	10.28 17.97	42.01 57.72			

Table 3 – Single fiber tensile strength of carbon fiber specimens.								
Samples	Gauge length, L (mm)	Number of samples	Weibull shape parameter (m)	σ <sub>m</sub> (GPa)				
Untreated CF CF-POSS-CNT	20 20	100 100	5.78 4.43	4.73 4.73				

composites. Single fiber tensile testing results of brittle materials, such as carbon fibers, are usually difficult to analyze, which is due to the high scatter observed. Thus, the tensile strength data are often statistically analyzed with Weibull distribution function [8]. The results of the fiber tensile testing are presented in Table 3. From Table 3, it can be seen that the grafting of POSS and CNTs on the carbon fiber surface does not lead to any discernable decrease in fiber tensile strength. The tensile strength of both untreated carbon fibers and hybrid reinforcements are 4.73 GPa. However, it should be noted that the Weibull shape parameter decreased slightly, which showed the scatter degree of the fiber tensile strength increased. Basically, lower the Weibull shape parameter is, more defects the fibers have. The oxidation and grafting reactions introduced some defects on the fiber surface although the fiber tensile strength did not have an obvious decrease. The results of the single fiber tensile testing imply that the functionalization would not lead to any discernable decrease in the in-plane properties of the resulting composites reinforced by the hybrid reinforcements.

## 3.5. Interfacial property testing

Short-beam bending tests and impact toughness tests were performed to evaluate the interfacial strength of the composites. The ILSS and impact toughness results of the composites reinforced by different carbon fibers are shown in Fig. 5. From Fig. 5a, it can be clearly seen that the grafting of POSS and CNTs significantly enhanced the interfacial adhesion of the composites. The ILSS increased from 80.8 MPa for the untreated carbon fibers to 95.4 MPa for the POSS grafted fibers by 18.1%. After POSS grafting, the epoxy functional groups on the POSS side chains play an important role in improving the interfacial adhesion between the fibers and the matrix. These polar functional groups could increase the surface energy of the carbon fibers, and make the fiber surface less hydrophobic and easier to be wetted by epoxy, which maximized the degree of the molecular contact. In addition, these epoxy groups could form strong chemical bonding at the interface of the composites by reacting with the amine hardener in the matrix during curing process. For the hybrid reinforcement reinforced composites, the ILSS further increased from 95.4 to 110.2 MPa by 15.5%. The further improvement on the interfacial strength could be attributed to the enhancement of the mechanical interlocking and the increased fiber surface area caused by CNTs on the fiber surface. These CNTs grafted on the fiber surface stick into the epoxy matrix and work as an anchor to locally stiffen at the interface region. In addition, the amine groups on the CNT end caps are also beneficial to increase the interfacial adhesion by reacting with the epoxy matrix during curing process.

The impact property tests were carried out to examine the effect of the POSS and CNT grafting on the impact resistance of the composites. As shown in Fig. 5b, the initial, propagative and total absorbed energy of the untreated carbon fiber composites were 1.13, 0.11 and 1.24 J, respectively. After being grafted with POSS, the initial, propagative and total absorbed energy of the composites surprisingly increased to 1.32, 0.66 and 1.98 J, respectively. Generally, a simplex enhanced interfacial adhesion usually means an increased interfacial strength but a simultaneous decreased material toughness, since too strong interfacial adhesion can limit the energy absorption and make the composites more brittle. However, through optimizing the interphase structure, the interfacial strength and toughness could be simultaneously improved. In this research, the increased composite impact toughness could be mainly contributed to the presence of the POSS interphase. When the composites are under load, the cracks in the matrix propagate to the fibers, and the direction of the crack propagation is decided by the stress field of the crack tip and the mechanical properties of the interphase and the fibers. The POSS interphase worked as a shielding layer which could relieve the stress concentration, prevent the crack tips to directly contact with the fiber surface and make the crack path deviate away from the fiber surface to the interphase region. In addition, numerous POSS nanoparticles on the fiber sur-



Fig. 5 – (a) ILSS and (b) impact toughness of the composites reinforced by untreated and grafted carbon fibers.

face could induce more cracks when the major crack passed to them, which could efficiently absorb the fracture energy. Moreover, the large numbers of the flexible glycidyldimethylsilyl side chains of POSS were also beneficial to increase the impact resistance by restricting the crack tip propagation and blunting the crack tip. However, it should be noted that



Fig. 6 – Results of DMA testing performed to simulate actual application environment and evaluate the effect of the functionalization on the mechanical property of the composites under dynamic load.

after CNT grafting, although the impact resistance increased compared with the untreated specimens, the testing results slightly decreased compared with the POSS grafting ones. The initial, propagative and total absorbed energy of the composites were 1.29, 0.36 and 1.65 J, respectively, which were mainly due to the further enhanced interfacial strength caused by the CNTs. The tighter interfacial bonding led to a higher stress concentration at the interphase, which resulted in the slightly decreased impact resistance. So according to different applications, a balance of the resulting composite properties between the interfacial adhesion and impact resistance should be considered.

# 3.6. DMA testing

The mechanical properties of composites under dynamic load were characterized by DMA, which could simulate the actual application environment of the composites. The variations of the storage modulus (E') and the tan $\delta$  with temperature for the composites reinforced by different carbon fibers are shown in Fig. 6. The results indicate that E' for the composites reinforced by the hybrid reinforcements is higher than that of the untreated fibers. As shown in Fig. 6, E' increased from 56 to 67 GPa below glass transition temperature (T<sub>g</sub>) and from 2.9 to 5.2 GPa above T<sub>g</sub>. The presence of hybrid reinforcements enables the composites to sustain stiffness at higher temperature



Fig. 7 – Interphase modulus testing results. (a) AFM force modulation image, (b) section analysis of the interphase in traditional carbon fiber composites, (c) AFM force modulation image, (d) section analysis of the interphase in POSS and CNT grafted carbon fiber composites.

near  $T_g$ . This may be due to the better interfacial adhesion between matrix and reinforcements, which can bring an increase in the volume fraction of interphase in the composites and a decrease in the effective polymer chain mobility at the interphase region. This interphase area could work as an additional reinforcement for mechanical stiffening of the composites [28].

 $T_{\rm g}$  is identified as a maximum in the tan $\delta$  curves. The untreated fiber composites had a  $T_{\rm g}$  of 138 °C.  $T_{\rm g}$  of the composites reinforced by the hybrid reinforcements shifted toward higher temperature, about 17 °C higher than that of the untreated ones. In addition, the peak intensity of the modified carbon fiber composites was decreased compared with that of the untreated carbon fiber composites. The increase of  $T_{\rm g}$  probably may be due to the enhancement of a restricted-mobility interphase region. The epoxy groups of POSS and the amine groups on the CNT end caps can increase the resin wettability and react with the matrix, which increases the crosslink density of the interphase region. Moreover, in the glass transition region, the CNTs in the interphase region hinder the viscous flow of epoxy chains and decrease the energy loss of the viscous deformation.

### 3.7. Interphase modulus testing

The force modulation AFM was used to characterize the local mechanical properties of the interphase region, which allows a qualitative statement about the local modulus of sample surface using an oscillating cantilever tip which indents into the sample surface. In accordance with the local modulus of the sample, corresponding cantilever amplitude will change under scanning. On the stiff areas of the sample surface, the depth of indentation will be smaller, and on the compliant areas larger. So the different response of the cantilever from areas with different modulus can be observed [29,30].

The force modulation images obtained from the cross-section of the composites reinforced by different carbon fibers are shown in Fig. 7. Notice that there are striking differences between the force modulation images. Fig. 7a shows apparent contrast between the fiber and matrix region. Obvious interphase region is not found and modulus sharply changes from the carbon fiber to the matrix region (Fig. 7b). The crosslink of the matrix was not affected by the fiber surface. Compared with Fig. 7a, the force modulation image of the hybrid reinforcement reinforced composites (Fig. 7c) shows obvious contrast among the fiber, interphase and matrix region, revealing a difference in the mechanical properties of these three regions. The interphase shows a moderate modulus, which is lower than that of the fiber and higher than that of the matrix. From the section analysis image (Fig. 7d), it can be obviously observed that a distinct modulus transition region corresponding to the interphase exists. The change of the modulus near the fiber surface could be attributed to the increased crosslink density of the matrix at the interphase through reacting between the matrix and the organic groups of POSS. This interphase in the composites is similar to biological systems, which rarely exhibit discrete boundaries between two materials with vastly different mechanical properties. The gradient modulus makes the interphase acts

as a stress transfer medium and the load can be transferred from matrix to carbon fibers uniformly.

# 4. Conclusions

Octaglycidyldimethylsilyl POSS and CNTs were uniformly grafted on the carbon fiber surface in an attempt to improve the interfacial properties between carbon fibers and an epoxy matrix. The roughness and polar functional groups of the carbon fiber surface increased obviously after modification. The surface energy also increased significantly. The grafting reaction did not lead to any discernable decrease in fiber tensile strength. Both the ILSS and the impact resistance had dramatic increases compared with the untreated fiber composites. In addition, the dynamic mechanical property of the composites also enhanced significantly. The functionalization effectively improves the interfacial adhesion of the composites not only by using the epoxy groups on the POSS side chains to increase the resin wettability and participate in the interfacial reaction, but also increasing mechanical interlocking caused by the CNTs grafted on the fiber surface. Moreover, the interphase with a gradient modulus and a thickness of several tens of nanometers can effectively transfer stress and reduce stress concentrations. With the recent acceptance of composites in commercial aircraft and autos, this hybrid reinforcement could lead to significantly stronger and tougher materials which would advance the lifespan and safety of these structures. It is noticeable that this significantly improvement in the interfacial properties is obtained without any effort to optimize the process of the grafting reactions, so it is expected that the interfacial properties can be further increased. Moreover, the reactive groups of POSS, which can be further functionalized with other reactive molecules, give an ability to engineer the interphase based on the desired application.

### Acknowledgements

The authors gratefully acknowledge financial supports from the Chang Jiang Scholars Program and the National Natural Science Foundation of China (No. 51073047 and No. 51003021). We also acknowledge Mr. Kun Sun of SII Nano-Technology Inc. for assistance with DMA testing.

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