Enhanced mechanical properties and anti-hydrothermal ageing behaviors of unsaturated polyester composites by carbon fibers interfaced with POSS

Dawei Jiang^{1,2}, Lixin Xing¹, Li Liu^{1,*}, Shaofan Sun¹, Qingbo Zhang¹, Zijian Wu¹,
Xingru Yan², Jiang Guo,² Yudong Huang¹, Zhanhu Guo^{2,*}

1. School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin, China
2. Integrated Composites Lab (ICL), Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, TN, 37996, USA

*Corresponding author. E-mail: liuli@hit.edu.cn; zguo10@utk.edu

Abstract

Trisilanolisobutyl polyhedral oligomeric silsesquioxane (SO 1450 POSS) has been uniformly grafted on the carbon fiber (CF) surface and the surface roughness (108.4 nm) of the CFs grafted with POSS was higher than that of the as-received CFs (57.9 nm). Dynamic contact angle analysis of the SO grafted CFs showed higher surface energy than that of the as-received CFs. After grafted with SO, the interlaminar shear strength of the unsaturated polyester (UPR) composites was 61 MPa, increased by 29.8% compared with that of the composites with the as-received CFs (47 MPa). The interfacial shear strength (IFSS) of SO grafted CFs/UPR composites was 88 MPa, significantly increased by 91% compared with that of the as-received CFs/UPR composites (46 MPa). The IFSS of the SO grafted CFs/UPR composites after hydrothermal ageing was 74 MPa with a decrease of just 16% compared with that of the as-received CFs/UPR composites (30 MPa) with a significant decrease of 35%. The tensile strength of the SO grafted CFs/UPR composites (1280MPa) is 15% higher than that of the as-received CFs/UPR composites (1110 MPa). The impact energy of 1.52 J for the SO grafted CFs/UPR composites is higher than 1.00 J for the as-received CFs/UPR composites.

Keywords: A. Carbon fibres; A. Nano particles; B. Fibre/matrix bond; B. Interphase; B. Mechanical properties

1. Introduction

The carbon fibers (CFs) reinforced polymer matrix composites have been used in many areas including aerospace, marine and automobile industries due to their excellent mechanical properties and low weight compared to traditional metal materials [1, 2]. The CFs reinforced polymer matrix composites possess three parts including reinforcing CFs, hosting matrix and interphase between CFs and matrix. This interface between the fiber and the matrix makes a critical contribution to the performance of the composites and a good quality interface can result in good mechanical properties [3-5]. In recent years, many researchers focus on the modification of the interface between CFs and matrix using various methods such as physical coating treatment [6-8] and chemical grafting [9-15].

Unsaturated polyester resins (UPR) have been widely used due to their relatively low price, ease of handling and a good balance of mechanical and chemical properties, and have been a popular thermoset used as the polymer matrix in composites [16, 17]. Usually, UPR reinforced with unmodified CFs have low interlaminar shear strength, interfacial strength and are subjected to stress cracking and brittle fracture due to the smooth and inert characteristics of the CFs [18-21]. As the applications of CFs/UPR composites become more and more important, CFs surface modification is required.

One useful method is to graft nanoparticles on CFs surface to increase the surface wettability, roughness or chemical bonding for an increased the interfacial strength between CFs and UPR [22].

Polyhedral oligomeric silsesquioxanes (POSS) are organic–inorganic molecules,

approximately 1 to 3 nm in diameter, with a general formula $(\text{RSiO}_{1.5})_n$, where R is hydrogen or an organic group, such as alkyl, aryl or any of their derivatives [23]. Trisilanollsobutyl POSS (SO 1450) is a kind of POSS of its open-cage-like structure with an inorganic silsequioxane at the core, organic isobutyl groups attached at the corners of the cage and three active silanol functionalities. SO 1450 can be used for surface modification of fillers, such as metal oxides, and other materials. It is also effective as an additive to thermoplastics and thermoset polymers for improving the moisture resistance and process-ability [24, 25]. SO 1450 possesses several distinct advantages (providing thermal and chemical stability, enhanced compatibility with the hosting polymer matrix or with the functional groups for chemically reacting with a polymer matrix) over traditional surface modifiers like silanes due to its hybrid molecule. For example, Yuan et al. grafted traditional silane coupling agent to carbon fiber surface to increase the mechanical properties of the carbon fibers reinforced phenolic resin, however at the sacrifice of decreasing the single fiber tensile strength. Zhu et al. grafted epoxy monomer through traditional silane coupling agent to increase the tensile strength of the carbon fibers reinforced epoxy resin.[26-28]. Our previous researches have demonstrated that the chemical bonding on the interface of CFs/UPR composites rather than roughness and wettability played the most important role in enhancing the interface strength to improve the mechanical properties. Though the effects of roughness and wettability played a weaker role than chemical bonding with a slightly improved interface strength by 6.2% [18, 29], how to improve the mechanical properties significantly is not reported. Meanwhile, the anti-hydrothermal aging

behaviors of the UPR composites were not studied yet.

In this paper, a proper interface between CFs and UPR with the combined action of roughness, wettability and chemical bonding was created by chemical grafting SO 1450 on the CFs surface. After the SO 1450 grafted on the CFs, the CFs roughness and wettability were improved with the formation of Si-O-Si and Si-O-C bonds at the interface of CFs/UPR composites. These bonds can increase some special properties like anti-hydrothermal ageing because destroying the Si-O-Si and Si-O-C bonds needs strong acid, strong base and more energy. The SO 1450 was introduced onto the CFs by directly reacting with the hydroxyl group of the CFs. It is easier to graft SO 1450 on CFs surface than other nanoparticles with different functional groups, which need graft intermediates on the CFs first and then graft the nanoparticles through the intermediate [13, 18, 29-32]. And the effects of the SO 1450 on the interface of CFs/UPR composites were investigated. The surface functional groups and surface chemical composition of the CFs were characterized by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS), respectively. The surface morphologies of the CFs were observed by atomic force microscopy (AFM) and scanning electron microscope (SEM). The wettability and surface free energy of the untreated and functionalized fibers were investigated by dynamic contact angle analysis test (DCAT). The interfacial mechanical properties of the composites were characterized by short-beam bending test method (interlaminar shear strength, ILSS), single fiber pull-out test method (interfacial shear strength, IFSS), impact test method (impact toughness). The anti-hydrothermal ageing was characterized through IFSS. The tensile

properties of the unidirectional CFs/UPR composites were tested in the fiber direction by using universal mechanical machine. The micro-mechanism of the composite interphase region was investigated by force modulation atomic force microscopy (FMAFM).

2. Materials and experimental method

2.1 Materials

AROPOL MR13006 unsaturated polyester resins (UPR) and low shrinkage agent LP4016 (reducing the volume shrinkage of UPR curing) were supplied by Ashland Inc., USA. Tert-butyl peroxybenzoate (TBPB, 98% purity, ACROS ORGANICS Inc) was used as an initiator for UPR curing. NaBH₄ (98% purity) was purchased from Alfa Aesar. H₂SO₄ (98%), HNO₃ (68%) and tetrahydrofuran (THF) were purchased from Tianjin Dongli big chemical reagent factory. The un-sizing polyacrylonitrile (PAN) based carbon fibers (Chinese Carbon Fiber 300, CCF300) were obtained from WeiHai GuangWei Group (12×10³ single filaments per tow, tensile strength of 3.26 GPa, average diameter of 7 μm, density of 1.76 g cm⁻³, Shandong, China). The trisilanollsobutyl POSS (SO 1450) was obtained from Hybrid Plastics Co., Inc. and were used as received. The chemical structures of POSS, TBPB, UPR and un-sizing CFs are shown in [Fig. 1](#).

2.2 Grafting procedures

The CFs (4 g) were oxidized in a 3:1 (v/v) mixture of concentrated H₂SO₄/HNO₃ at 60 °C for 2 h, washed with deionized water until water was neutral. The oxidized CFs were then reduced in a solution of NaBH₄ (1.0 g) in 200 mL anhydrous ethanol at room

temperature for 20 h. The mixture was heated to 78 °C and maintained for 4 h. The products were washed with deionized water until the solution became neutral and then dried (the product is denoted as “CF-OH”). CF-OH was reacted with SO140 in 150 mL THF solution of 3.5 g SO 1450 at 65 °C for 12 h with mechanical stirring. The product was rinsed with excess THF to remove unreacted POSS, washed with deionized water until water became neutral, and then dried for other usages (the product is denoted as “CF-POSS”). The grafting of POSS on the surface of CFs is shown in Fig. 2.

2.3 Fabrication of CFs/UPR composites

The CFs reinforced UPR composites were prepared by compression molding method. The unidirectional prepreg carbon fibers were put into a mold to make composites. The detailed preparation description of the fiber prepreg is as follows. First, the fibers were wrapped around a metal frame with 11 circles. And then the resin solution of MR13006, LP4016 and TBPB used at a mixture ratio (weight) of 105:45:1 was made. The wrapped fibers were immersed into the resin solution for one hour and then the fibers were slightly rubbed till the resin was fully saturated into CFs. The prepreg fiber was completed. Briefly, the CFs/UPR composites were prepared by heating the samples at 80 °C for one hour without pressure, a pressure of 10 MPa was applied at 100 °C for one hour, then the sample underwent 140 °C for one hour under 10 MPa, finally the mold was cooled down to room temperature with the pressure being maintained. The resin content of the composites was controlled at 30±1.5 mass%. The specimen dimensions were 20 mm×6.5 mm×2 mm for interlaminar shear strength, the specimen dimensions were 55 mm×6.5 mm×2 mm for impact test and the specimens dimensions

were 250 mm × 15 mm × 1.0 mm for tensile strength test, respectively.

2.4 Characterization

The surface functional groups of the CFs were analyzed by Fourier Transform Infrared (FTIR) spectrophotometer (Nicolet, Nexus 670, USA) in Attenuated Total Reflectance (ATR) mode. Before the surface analysis, the CFs were dried for 2 h under vacuum at 150 °C. In order to obtain a good optical contact, a very thin KBr layer was introduced between the prism and the CFs by using a KBr pelletizer. The FTIR spectra were acquired by scanning the specimens for 64 times in the wavenumber range of 400–4000 cm⁻¹ with a resolution of 2 cm⁻¹.

X-ray photoelectron spectroscopy (XPS, ESCALAB 220i-XL, VG, UK) was carried out to study the surface element of the CFs using a monochromated Al *Kα* source (1486.6 eV) at a base pressure of 2×10⁻⁹ mbar. The XPS was energy referenced to the C1s peak of graphite at 284.6 eV. The XPS Peak version 4.1 program was used for data analysis. The treatment effects on the fiber surface morphology were observed by using FEI Sirion 200 scanning electron microscope (SEM, Royal Dutch Philips Electronics Ltd., Netherlands) and atomic force microscopy (AFM, Solver-P47H, NT-MDT, Russia). Individual fiber was examined in Solver P47 AFM/STM system (NT-MDT Co.). AFM was also used to investigate the microstructures of the composites. The force modulation mode was adopted to study the cross-section surfaces of unidirectional CFs/UPR composites and the relative stiffness of various phases, including the CFs, interface, and resin. The composites were first polished perpendicularly to the fiber axis using increasingly finer sand papers, and then with a Cr₂O₃ (50 nm) suspension, finally

washed with water under ultrasonication and dried for tests.

Dynamic contact angle and surface energy analyses between testing liquids (deionized water and diiodomethane, 99% purity Alfa Aesar, USA) and single fiber were performed using a dynamic contact angle tensiometer (DCAT21, Data Physics Instruments, Germany).

The interlaminar shear strength (ILSS) of the CFs/UPR composites was measured on a universal testing machine (WD-1, Changchun, China) using a three point short beam bending test according to ASTM D2344. The specimens were conditioned and an enclosed testing space was maintained at room temperature. The measurements were at a cross-head speed of 2 mm/min.

The impact tests were carried out in a drop weight impact test system (9250HV, Instron, USA). The impact span was 40 mm, the drop weight was 3 kg and the velocity was 2 m/s. Each reported data was an averaged value of 5 specimens.

A carbon fiber monofilament was fastened to a metal holder with adhesive tape. Some UPR droplets were applied to the monofilament with the embedded length of 60–80 μm using a fine-point applicator. The curing procedure was the same as that for the preparation of CFs/UPR composites. After curing, the interfacial shear strength (IFSS) was adopted to quantify the interfacial property between CFs and resin matrix by the interfacial evaluation equipment (Tohei Sangyo Co Ltd., Japan), at a crosshead displacement rate of $0.5\mu\text{m s}^{-1}$.

The curing procedure was the same as that for the preparation of CFs/UPR composites. The IFSS was also measured after the samples boiled in 100 °C water at

the time of 48 h for hydrothermal aging.

The tensile strength (TS) of a single filament was performed on an electronic mechanical universal material testing machine (Instron 5500R, USA) according to ASTM D 3379-75. A carbon fiber monofilament was adhered to a rectangular piece of paper with a rectangular hole in the middle of the paper. Before the test, the two long sides of the paper were cut. A gauge length of 20 mm and cross-head speed of 10 mm/min were used for all the fiber samples. At least, 60 specimens were tested for each fiber type, and then the average value was considered as the tested value. The tensile strength of the unidirectional CFs/UPR composites was performed by using an Instron 5985 machine according to the ASTM D3039 with a cross-head speed of 2 mm/min and a load cell of 250 kN. At least five specimens were tested for each type of composites. The obtained results are quoted as the average values with deviation from all tested specimens.

3. Results and discussion

3.1 Surface chemical elemental composition

Fig. 3(a&b) shows the FTIR spectra of the as-received and SO 1450 grafted CFs. The as-received CFs are observed to have the bending vibration of adsorbed water and the C–H stretching of methyl and methylene groups, few organic groups can be observed in the as-received fibers, **Fig. 3(a)**. For the POSS grafted CFs, the broad band at about 880 cm^{-1} corresponds to the Si–C stretching vibration, **Fig. 3(b)**. The bands at around 1055 cm^{-1} correspond to the Si–O–Si or Si–OH stretching vibrations. The band at 1102 cm^{-1} was assigned to the stretching vibration of C–O. The band at 1290 cm^{-1} corresponds to the asymmetric deformation vibration of the CH_2 of Si– CH_2 due to the

grafted POSS.

The surface composition of the as-received and grafted CFs was determined by XPS and the results are shown in Table 1. The as-received CFs surface only contains carbon, oxygen and a small amount of nitrogen. After being grafted with SO 1450, the carbon content was decreased from 82.03% for the as-received CFs to 71.48% and the oxygen content was increased from 16.86% for the as-received CFs to 22.65 % for the SO 1450 grafted CFs, and the silicon was observed with an element content of 4.74%. The surface atomic Si/C ratio was increased sharply from 0 to 0.07 for the SO 1450 grafted CFs. The C1s XPS spectra of the as-received and SO 1450 grafted CFs are shown in Fig. 3(c & d). The C1s spectrum of the as-received CFs shows 69.1% C–C, 21.6% C–O, 5.9% C=O and 3.4% O–C=O. The C1s spectrum of the SO 1450 grafted CFs shows 57.8% C–C, 35.9% C–O, 1.3% C=O, 3.7% O–C=O and 1.3% C–Si, respectively. Compared with the as-received CFs, the C–O was increased significantly from 21.6 to 35.9% for the SO 1450 grafted CFs and the C–Si was observed due to the introduced SO 1450 on the CFs surface. Both FTIR and XPS analysis confirmed the successful grafting POSS on CFs surface.

3.2 Surface topography and dynamic contact angle analysis of carbon fibers

The SEM images of the as-received and SO 1450 grafted CFs are shown in Fig. 4(a & b), respectively. The surface of as-received CFs has many shallow grooves parallel distributed along the longitudinal direction of the CFs, Fig. 4(a). The SO 1450 particles are observed uniformly distributed on the CFs surface, Fig. 4(b). The more accurate microscopic and 3-dimensional topographies of CFs surface were performed by AFM.

Fig. 4(c&d) shows the as-received and SO 1450 grafted CFs. The carbon fibers surface roughness, calculated from the plane topography images by using the AFM software, is shown in Table 2. The as-received CFs have many relatively neat shallow grooves arising from the production process with a small roughness of 57.9 nm. The CFs grafted with SO 1450 become much rougher (108.4 nm) due to the uniform POSS particles scattered on the surface and in the voids of the fiber grooves, Fig. 4(d).

The contact angle θ was determined from the mass change during the immersion of fibers in each test liquid, using Wilhelmy's Eq (1) [33]:

$$\cos\theta = \frac{mg}{\pi \cdot d_f \cdot \gamma_1} \quad (1)$$

where, d_f is the fiber diameter, g is the gravitational acceleration, and γ_1 is the surface tension of the test liquid. The surface energy (γ_f), dispersion component (γ_f^d) and polar component (γ_f^p) of the CFs were estimated from the measured dynamic contact angles of the test liquids with known surface tension components and were calculated according to Eq (2&3):

$$\gamma_1(1 = \cos\theta) = 2(\gamma_1^p \gamma_f^p)^{1/2} + 2(\gamma_1^d \gamma_f^d)^{1/2} \quad (2) \quad \gamma_f = \gamma_f^p + \gamma_f^d \quad (3)$$

where, γ_1 , γ_1^d and γ_1^p are the liquid surface tension, its dispersion and polar component, respectively. Deionized water ($\gamma^d=21.8 \text{ mJ}\cdot\text{m}^{-1}$, $\gamma=72.8 \text{ mJ}\cdot\text{m}^{-1}$) and diiodomethane ($\gamma^d=50.8 \text{ mJ}\cdot\text{m}^{-1}$, $\gamma=50.8 \text{ mJ}\cdot\text{m}^{-1}$, 99% purity, Alfa Aesar, USA) were used as the test liquids. Each measurement was repeated 5 times and the results were averaged. In this work, the surface wettability of the CFs was evaluated via a Cahn dynamic angle analysis system. The θ , γ , γ^d and γ^p of the as-received and SO 1450 grafted CFs are summarized in Table 2. As shown in Table 2, after grafted with SO

1450, the θ was decreased to 30.2° from 74.39° for polar water, and was increased to 59.33° from 56.31° for non-polar diiodomethane. The γ_f was obviously increased, and the γ^d and γ^p components of SO 1450 grafted CFs were 28.98 and 35.80 mJ·m⁻¹, respectively. The γ_f of the SO 1450 grafted CFs was calculated to be 64.76 mJ·m⁻¹, significantly higher than that of the as-received CFs. The increased surface energy was due to the introduction of high polar functional group (Si-OH) on the CFs surface and the increased surface energy could effectively improve the wettability between the fibers and the resin.

3.3 Interfacial property testing

The force modulation AFM (FAFM) was used to characterize both surface topography and hardness diagram. The force modulation images of the interphase region between CFs and UPR matrix were shown in Fig. 4(e&f). The clear interface region is observed after the SO 1450 grafted on the CFs, Fig. 4(e), however only two phases are observed for the as-received CFs reinforced UPR composites, Fig. 4(f). A uniform interface layer is formed due to the formation of Si-O-Si and Si-O-C bonds at the interface of CFs/UPR composites. There is a transition region (Fig.4f), at which the color is different from the matrix and the reinforcement, i.e., a little darker than matrix and a little lighter than reinforcement. This phenomenon can be seen clearly in Fig.4f between CF and UPR. If there is an interphase, there would be a stiffness difference between matrix and reinforcement. The relative stiffness is indirectly indicated by the detection of magnitude (MAG, in units of nA) of the flexural quantum of the microcantilever. There are obviously different stiffness phases, i.e., CF, interphase and UPR, on the cross-section surface of the composites. The stiffness of interphase is higher than that of

the UPR and lower than that of the CF.

Oxidation and grafting treatment will unavoidably introduce defects on the surface of fibers, which could decrease the fiber strength. However, compared with the strength of the as-received CFs (3.26 GPa), comparable fiber tensile strength is observed for the CFs grafted with SO 1450 (3.27 GPa). The strength of a single carbon fiber obeys the single Weibull distribution, i.e., the lower the Weibull shape parameter is, the more defects the fibers have. The tensile strength of a single fiber does not show discernable decrease although the defects were introduced after grafting. The results of the single fiber tensile test suggest that the chemical grafting of POSS on the fibers has no significant effects on the fiber tensile strength.

The interlaminar shear stress is important since it has a significant effect on the failure strength of the composite laminate. The interlaminar shear strength (ILSS, Γ) of the as-received and grafted CFs reinforced UPR composites has been characterized by short-beam bending tests to evaluate the interface strength of the composites. The Γ for the short-beam test was calculated according to Eq. (4) [34].

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

where P_b is the maximum compression force at fracture in Newton, b is the width of the specimen in mm, and h is the thickness in mm. Each reported Γ value was averaged for more than eight successful measurements. Fig. 5(a) shows the ILSS of the as-received, and SO 1450 grafted CFs reinforced UPR composites. The grafted fiber composites have higher ILSS (61 MPa) than that of the as-received fiber composites (47 MPa), an

increase of 29.8% due to the combined effects of the enhanced mechanical interlocking, wettability and the introduced chemical bonding at the interface of the composites. The interfacial strength (IFSS) of CFs/UPR composites was calculated, Eq (5) [35],

$$IFSS = \frac{F_{max}}{\pi d_f l_e} \quad (5)$$

where F_{max} is the maximum load recorded, d_f is the carbon fiber diameter, and l_e is the embedded length of carbon fiber in the UPR. As shown in Fig. 5(b), the IFSS of SO 1450 grafted CFs is observed to have a higher value of 88 MPa, an increase of about 91% in comparison with that of the as-received CFs (46 MPa).

Fig. 5(c) shows the impact property testing results of the composites reinforced with the as-received and POSS grafted CFs. The initial, propagative, and total absorbed energy of the as-received CF composites were 0.21, 0.79 and 1.00 J, respectively. After modification, the impact toughness is increased significantly for the composites containing SO 1450 grafted CFs. The initial, propagative, and total absorbed energy were 0.93, 0.59 and 1.52 J for the composites with CFs grafted with SO 1450, respectively. The results indicate a higher impact strength (1.52 J) than that without POSS grafted CFs (1.00 J). When the impact force is applied to the composites, the interface between CFs and UPR matrix serving as a shielding layer induces more cracks to prevent the crack tips to directly touch the CFs reinforcement that can efficiently absorb the fracture energy, resulting in an increased initial absorbed energy.

3.4 Tensile properties of unidirectional CFs/UPR composites

To further understand the combined effects of the enhanced mechanical interlocking, wettability and the introduced chemical bonding at the interface of the composites for

the SO 1450 grafted CFs, the tensile strength of the unidirectional CFs/UPR composites was investigated by tensile test. Fig. 5(d) shows the tensile strength of the composites reinforced with the as-received and modified CFs. The tensile strength of the SO 1450 grafted CFs composites (1280 MPa) is 15% higher than that of the as-received CFs composites (1110 MPa), Fig. 5(d). This increase is due to the introduction of SO 1450 nanoparticles on the CFs surface. The fiber surface nanostructures were altered by the SO 1450. The SO 1450 is the hybrid molecule with an inorganic silsequioane at the core, organic isobutyl groups attached at the corners of the cage and three active silanol functionalities. After the SO 1450 grafted on CFs surface, the roughness, surface energy, and chemical reaction of the CFs were significantly improved. These improvements enhanced the mechanical interlocking and chemical interlocking at the interface of the composites to give an enlarged tensile strength.

3.5 Hydrothermal ageing of composites

The hydrolysis and damage of the interface could decrease the mechanical properties of the composites. To better understand the role of SO 1450 in the enhancement of the interface in the composites, the hydrothermal ageing of the composites was investigated through the micro-composites boiling in the 100 °C for 48 h. Fig. 5(b) shows the IFSS of the CFs/UPR composites after ageing. The as-received CFs/UPR composites after ageing have a IFSS value of 30 MPa, as compared with the as-received CFs/UPR composites before ageing (46 MPa), a significant decrease of 35%. However, for the SO 1450 grafted CFs/UPR composites after ageing with a IFSS of 74 MPa, there is just 16% decrease. The Si-O-Si and Si-O-C bonds have been formed at the interface of the

CFs/UPR composites after the SO 1450 grafted CFs, however, there is no bond formation between the as-received CFs and the resin. The damage of the Si-O-Si and Si-O-C bonds needs strong acid, strong base and more energy [36-38]. So better anti-hydrothermal ageing for the SO 1450 grafted CFs is due to the enhanced interface.

3.5 Interface property of the impact fracture surfaces of composites

Fig. 6(a&b) shows the impact fracture surface of the composites. For the as-received CFs/UPR composites, **Fig. 6(a)**, a lot of fibers were pulled out from the UPR matrix in a large area. The obviously observed interface de-bonding between CFs and UPR matrix and big holes in the matrix indicated a weak interfacial adhesion. After grafted with SO 1450, few fibers were pulled out and the pull-out length of the fibers was very short due to the enhanced mechanical interlocking, wettability and the introduced chemical bonding at the interface of the composites, further confirming an improved interface between CFs and UPR matrix, consistent with the FMAFM, IFSS, ILSS and tensile test.

4. Conclusion

SO 1450 was uniformly grafted on the CFs surface and effectively enhanced the mechanical and anti-hydrothermal ageing properties of the CFs and UPR composites. The wettability and roughness of the CFs grafted with SO 1450 were improved compared with the as-received CFs. For the grafted CFs/UPR composites, the ILSS (61 MPa), IFSS (88 MPa), impact energy (1.52 J), tensile strength (1280 MPa) and anti-hydrothermal ageing were dramatically increased compared with that of the as-received CFs/UPR composites (47, 46 MPa, 1.43 J and 1110 MPa). Moreover, from the FMAFM and SEM observations of the impact fracture surfaces, a better interfacial

adhesion between the CFs grafted with SO 1450 and the resin was observed. The improved interfacial strength for the SO 1450 grafted CFs/UPR composites was attributed to the combination of three factors: (1) the enhanced mechanical interlocking, (2) the improved wettability of the CFs and (3) the chemical bonding on the interface. The chemical bonding on the interface of CFs/UPR composites can also improve the anti-hydrothermal ageing behaviors.

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Table 1. Surface chemical composition of CFs with and without POSS grafted.

Carbon fibers	Element content (at%)					
	C	O	N	Si	O/C	Si/C
As-received CFs	82.03	16.86	1.1	—	0.20	—
CF–trisilanollsobutyl POSS	71.48	22.65	1.13	4.74	0.32	0.07

Table 2. Contact angle, surface energy and roughness of CFs with and without POSS.

CF	Contact angle (°)		Surface energy (mJ·m ⁻¹)			Ra (nm)
	Water	Diiodomethane	γ^d	γ^p	γ	
As-received CFs	74.39	56.31	23.82	10.64	34.46	57.9±1.1
CF–trisilanollsobutyl POSS	30.20	59.33	28.96	35.80	64.76	108.4±4.0

Fig. 1. Chemical structure of (a) trisilanollsobutyl POSS, (b) TBPB, (c) UPR, and image of un-sizing CFs. **Fig. 2.** Schematic illustration of the grafting procedures, not to scale.

Fig. 5. (a) Tensile strength of single fiber and ILSS, (b) IFSS before and after hydrothermal aging, (c) impact test, (d) tensile strength of composites reinforced with the as-received and modified CFs, and (e), (f) Weibull probability plot of single fiber tensile strength of the as-received and modified CFs.

Fig. 6. Morphologies of the fractured surface of CFs/UPR composites with (a) as-received, and (b) SO 1450 grafted CFs.