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Improved Interfacial Properties of Carbon Fiber/Unsaturated Polyester Composites Through Coating Polyhedral Oligomeric Silsesquioxane on Carbon Fiber Surface

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Abstract: Carbon fibers were coated with E51 plus Methacryl-POSS together in an attempt to improve the interfacial properties between carbon fibers and unsaturated polyester resins matrix. Atomic force microscopy (AFM), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) were performed to characterize the changes of carbon fiber surface. AFM results show that the coating of E51 plus POSS significantly increased the carbon fiber surface roughness. XPS indicates that silicon containing functional groups obviously increased after modification. Dynamic mechanical analysis was carried out to investigate the surface energy of carbon fiber. Force modulation atomic force microscopy (FMAFM) and Interlaminar shear strength (ILSS) were used to characterize the interfacial properties of the composites. ILSS was increased by 21.9 % after treatment.

Keywords: Carbon fiber, Unsaturated polyester, Interfacial properties, Surface treatments

Introduction

It is widely known that carbon fibers are mainly used as reinforcements in composites, which are widely used in aerospace, enginery, marine and automobile industries due to their outstanding properties such as preeminent mechanical strength and stiffness, lower density, flexible designs and chemical stability [1-6]. The carbon fiber, the resin matrix and the interphase formed between the two constituents influence the properties of the composites [7]. However, when applied without previous surface modification, the physicochemical interaction between carbon fibers and its reinforced matrix is not tough enough due to the inert surface properties of carbon fibers, which will directly affect interfacial adhesion in the composites [8-12]. As a result, vast masses of the surface treatment of carbon fiber have been investigated in order to improve their interfacial adhesion, such as electrochemical oxidation treatment [13], plasmas treatment [14], coating treatment [15-17] and so on.

Hybrid materials containing both inorganic and organic components are expected to have increased performance capabilities relative to their non-hybrid materials. Due to the nano-length scale involved, nano-composite materials feature an extensive array of interfacial interactions that can result in salient changes relative to their components' properties [18-20]. Polyhedral oligomeric silsesquioxane (POSS) reagents, monomers, and polymers are emerging as a new chemical technology for the nano-reinforced organic-inorganic hybrids and POSS compounds have $(SiO_{1.5})_n$ core cage structures where n=8, 10, or 12 with sizes from 1 to 3 nm in diameter. Organic substituents attached to each cage Si atom can improve compatibility with the polymer matrix [21,22]. The incorporation of POSS moieties into a polymeric material can dramatically improve its mechanical properties (e.g., strength, modulus, rigidity) as well as reduce its flammability, heat evolution, and viscosity during processing. These enhancements apply to a wide range of commercial thermoplastic polymers, high-performance thermoplastic polymers, and thermosetting polymers [23-26].

Unsaturated polyester resins (UPR) are extensively used in composite industry because of their good mechanical properties, low cost and low density, which are generally formed by a condensation reaction between a glycol and an unsaturated dibasic acid [27,28]. UPRs are frequently used as polymer matrix in glass-fiber reinforced composites, for example, in automotive or railway applications, however, they are hardly used as polymer matrix in carbon fiber reinforced composites due to it is bad compatibility with carbon fiber and the interlaminar property of CF/UPR composites is very low. So if we want to fabricate high performance of CF/UPR composites that can be used as automotive parts or other field, we should to modify the surface properties of carbon fiber [29].

In previous work, we had successfully enhanced the interfacial properties of carbon fiber/polyarylacetylene (CF/PAA) composites by using different silsesquioxane coating [15,30-33]. But we just only deposited the single coating on the fiber surface. In the present work, we researched the synergy effects of two kinds of coating according to the different properties between CF and UPR. We also researched

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the interfacial properties of CF/UPR composites. Force modulation atomic force microscopy confirmed the existence of the interface. The fiber surface composition and functional group were examined by using X-ray photoelectron spectroscopy (XPS). The surface morphology of the fiber was observed by atomic force microscopy (AFM) and scanning electron microscopy (SEM). The interfacial mechanical properties of the CF/UPR composites were characterized by short-beam bending test method.

Experimental

Materials

AROPOL MR13006 polyester (supplied by Ashland Inc., USA) had been used as matrix material for reinforced composites in our experimental work. Tert-Butyl peroxybenzoate (TBPB, 98 % purity) was purchased from ACROS ORGANICS Inc, which was used as initiator. Un-sizing Polyacrylonitrile (PAN) based carbon fibers (CCF300) were obtained from WeiHai GuangWei Group (12×10^3 single filaments per tow, tensile strength was 3.26 GPa, average diameter was 7 μm, density was 1.76 g cm^{-3}). (Shandong, China). Methacryl-POSS was bought from Hybrid Plastics Co., Inc. (Texas), and was used as received. Its structure is shown in Figure 1. Analytically pure tetrahydrofuran (THF) was purchased from the First Factory of Chemical Agents (Tianjin, China). Epoxy resin (E-51; molecular weight=350-400) was obtained from Xingchen Chemical Wuxi Resin Factory (Wuxi, China). Methyl tetrahyelrophthalic anhydride (METHPA) hardener was supplied by Sinopharm Chemical Reagent Co., Ltd.

CF Surface-coating Treatments and Preparation of the CF/UPR Composites

THF solutions of POSS (2 mass %) and E-51 (1 mass %, E51:METHPA=1:0.7) were prepared for the coatings, respectively. CF was wound on a rectangular metal frame and the number of circle was recorded for calculating the content of the resin. Then putting rectangular metal frame into a glass container filled with coating solution. One coating method was that the prepared solution was treated by ultrasonic for 10 minutes to coat POSS and E-51 uniformly onto the fiber surface, respectively and then the fiber was dried at 80° C for 0.5 h. Another method was that first CF was coated with E-51 by the same method but the ultrasonic

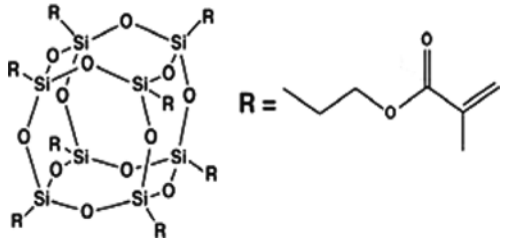

Figure 1. Structure of Methacryl-POSS.

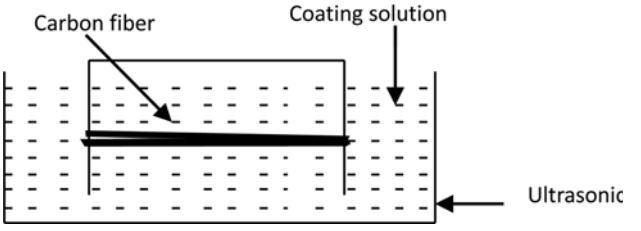

Figure 2. Schematic process of CF coating treatment.

time was decreased to 3 minutes so that a very thin layer of epoxy resin was coated onto fiber surface, then putting the sizing CF into POSS coating solution to coat CF surface for 5 minutes, which was also treated by ultrasonic, then the fiber was dried at 80 °C for 1 h. Carbon fiber coating treatment method was shown in Figure 2. The unidirectional and long CF reinforced UPR composites were made with both untreated and treated CF. Curing was performed on a compression-molding machine by compression molding. The content of the resin in the composites was controlled to be about 30 mass %.

The curing process was at 80 °C for 1 h without pressure and then the pressure was loaded to 10 MPa, 100 °C for 1 h under 10 MPa, and 140 °C for 1 h under 10 MPa, then the mold was cooled to room temperature with the pressure being maintained.

Characterization of Carbon Fibers

The effects of the treatment on the fiber surface morphology were observed by using atomic force microscopy (AFM) and scanning electron microscopy (SEM). Individual fiber was examined in Solver P47 AFM/STM system (NT-MDT Co., Russian) and S4700 SEM (HITACHI, Japan), respectively. During the process of AFM test, all images were obtained in semi-contact mode (tapping mode), which was more suitable for scanning the arched surface of a carbon fiber than the contact mode. During the process of SEM testing, the samples were metalized with a thin layer of platinum, 10 nm in thickness.

XPS (ESCALAB 220i-XL, VG, UK) was carried out to study surface element of carbon fibers using a monochromated Al Ka 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.

Dynamic contact angle and surface energy analyses were performed using a dynamic contact angle meter and tensiometer (DCAT21, Data Physics Instruments, Germany). The advancing contact angle was determined from the mass change during immersion of the fiber into each test liquid using Wilhelmy's equation:

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

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^p) and polar component (γ_f^d) of the carbon fibers were estimated from the measured dynamic contact angles of the test liquids with known surface tension components and calculated according to the following equations:

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

$$\gamma_f = \gamma_f^p + \gamma_f^d \quad (3)$$

Where, γ_1, γ_1^d and γ_1^p are the liquid surface tension, its dispersion and polar component, respectively. Deionised water (γ^d=21.8 mJ·m^{-1}, γ=72.8 mJ·m^{-1}) and diiodomethane (γ^d=50.8 mJ·m^{-1}, γ=50.8 mJ·m^{-1}, 99 % purity, Alfa Aesar, USA) were used as test liquids. Each measurement was repeated 5 times and the results were averaged.

Interfacial Characterization of the CF/UPR Composites

Force modulation AFM (Solver-P47H, NT-MDT, Russia) was used to investigate the micromechanism of the composite interphase region. The force modulation mode was adopted to study the cross-section surfaces of unidirectional CF/UPR composites and the relative stiffness of the various phases, including the CFs, interface, and resin. The composite specimens were firstly polished perpendicularly to the fiber axis using increasingly finer sand papers, and then polished with a Cr_2O_3 suspension of an average grain size of 50 nm, finally cleaned with water in an ultrasonic washer and dried.

The interlaminar shear strength (ILSS) of the CF/UPR composites were measured on a universal testing machine (WD-1, Changchun, China) using a three point short beam bending test method according to ASTM D2344. Specimen dimensions were 20×6×2 mm, with a span to thickness ratio of 5. The specimens were conditioned and an enclosed space where the test was conducted was maintained at room temperature. The specimens were measured at a rate of cross-head movement of 2 mm/min. The ILSS, for the short-beam test was calculated according to the following equation.

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

Where, Γ is the interlaminar shear strength, P_b is the maximum compression force at fracture in Newton, b is the breadth of the specimen in mm, and h is the thickness of the specimen in mm. Each ILSS value reported was the average of more than eight successful measurements.

Results and Discussion

Surface Topography of Carbon Fibers

The SEM images of untreated carbon fiber, E-51 coating, Methacryl-POSS coating and E-51 plus Methacryl-POSS coating are shown in Figure 3(A)-(D), respectively. The surface of untreated CF has many shallow grooves that are parallel distributed along with the longitudinal direction of the carbon fiber (as shown in Figure 3(A)), which is the typical morphology of CCF300 carbon fiber. After the E-51 being coated, a layer of E-51 appear and the most grooves are filled with coating, As shown in Figure 3(C), on the surface of CF-POSS, a layer of POSS particles appear and the carbon fiber becomes much rougher, however, the surface of CF-E51-POSS has more particles, which due to the E51 that like glue can make more POSS stick on the fiber surface. The rougher surface and more particles sticking into the composite interface region could significantly increase the interfacial adhesion by increasing fiber surface area and enhancing mechanical interlocking between the fiber and the matrix. From the SEM we can just observe the whole, flat and macroscopical topographies of CF surface. If we want to observe the more accurate microscopic and three-dimensional topographies of CF surface, we could by means of AFM.

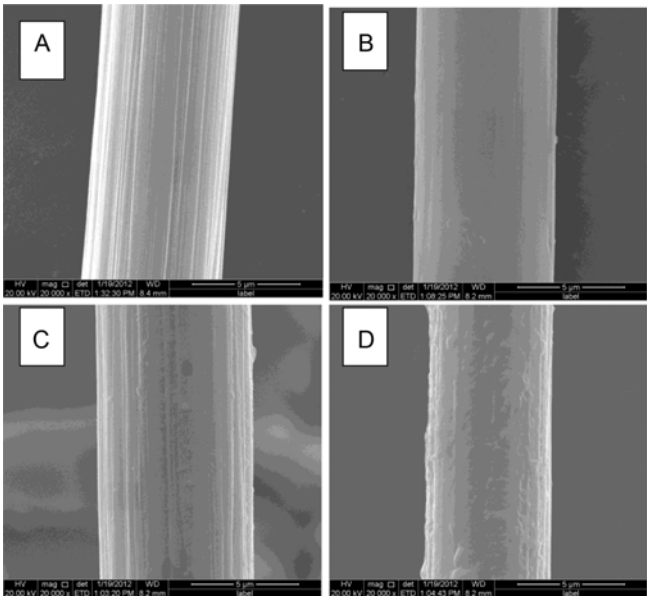

Figure 3. SEM topographies of CF in dierent coating treatment, all samples were washed with THF before observation (A) untreated, (B) E-51 coating, (C) Methacryl-POSS coating, and (D) E-51+ Methacryl-POSS coating.

The AFM three-dimensional topographies of CF were shown in Figure 4. The carbon fiber surface roughness was calculated from the plane topography images by using the AFM software is shown in Table 1.

By comparing the three-dimensional AFM topography images of the carbon fibers, remarkable differences of the surface topography between the untreated and modified carbon fibers can be observed. After coated, the surface topography on a microscopic scale is changed. Figure 4 shows that the surface of the CF is the same as that of SEM

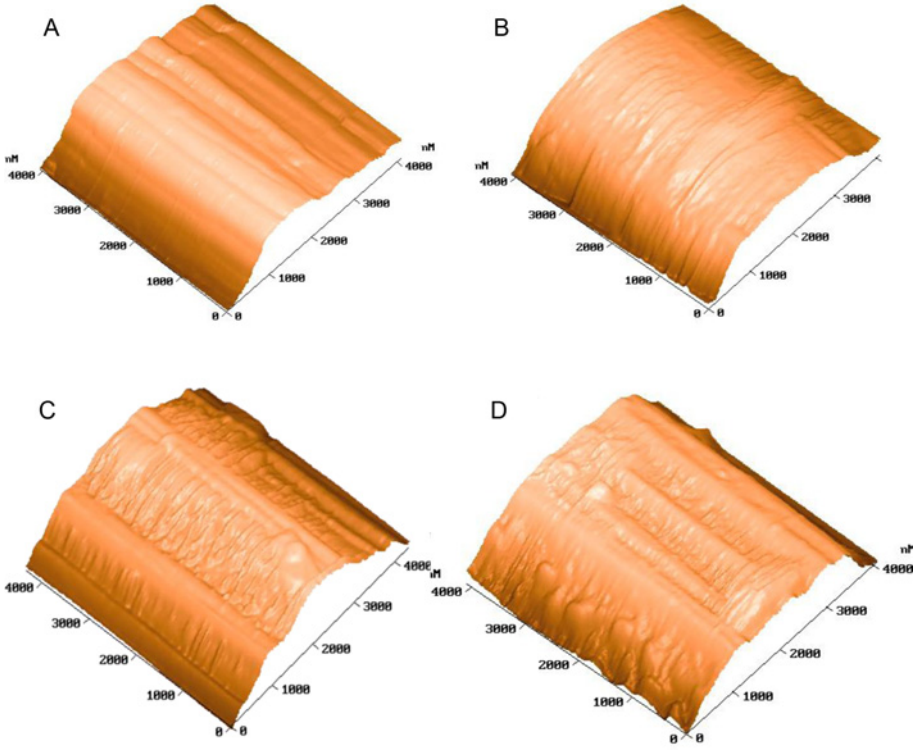

Figure 4. AFM images of different carbon ber surface, all samples were washed with THF before observation (A) untreated, (B) E-51 coating, (C) Methacryl-POSS coating, and (D) E-51+Methacryl- POSS coating.

Table 1. Roughness of CF with different coating

Samples	Ra (nm)
Untreated CF	56.8
POSS coating CF	75.1
E-51 coating CF	82.1
E-51+POSS coating CF	121.1

Table 2. Surface element analysis of carbon fibers

CF (at%)	C (%)	O (%)	N (%)	Si (%)
Untreated CF	81.04	15.83	2.43	0.70
POSS coating CF	60.63	34.00	0.68	4.69
E-51 coating CF	66.19	30.16	2.80	0.85
E-51+POSS coating CF	70.88	21.36	2.85	4.91

morphology, which the surface of untreated CF has many shallow grooves. After coated with Methacryl-POSS and E51, there are a number of streaks dispersed uniformly on the sized carbon fiber surface, which was formed by these coating. After E-51 plus Methacryl-POSS coating treatment, there are some obvious raised particles on the CF surface. These raised particles may be caused by E51 and the E51 can make Methacryl-POSS to stick on the surface of CF. Meanwhile surface roughness (SR) is changed dramatically after the coating treatment. The untreated CF surface roughness is 56.8 nm, which was the lowest one and the highest one among them is 121.1 nm which is coated by E-51 plus POSS. Both SEM and AFM topographies (Figures 3 and 4) also proved that there is a coating on carbon fibers surface. Thus, there is a bridge made from E-51 plus Methacryl-POSS between carbon fiber and UPR resin in composites, which could also be proved with XPS analysis.

XPS was performed to determine the chemical composition of the carbon fiber surface [34]. The surface composition of untreated and treated carbon fiber was determined by XPS and the results are given in Table 2. Table 2 provided the surface elements content of carbon fiber that is atomic concentration. Usually, there is only a small amount of oxygen on the untreated carbon fiber surface [34]. However, it should be noted that 15.83 % oxygen was detected on the untreated fiber surface, because CF was oxidized in process of fabrication. After coating treatment, the content of element was changed. After coated with Methacryl-POSS, the carbon content decreased from 81.06 % to 60.63 % and the oxygen content increased significantly from 15.83 % to 34.00 %. In addition, significant silicon element of 4.69 % was detected on the fiber. After E51 together with Methacryl-POSS coating treatment, silicon element increased a little from 4.69 % to 4.91 %.

As is known, chemical composition and topography of fiber surface can affect the fiber surface energy as well as its

Table 3. Surface energy of treated and untreated CF

CF	Contact angle (°)		Surface energy (mJ·m^{-1})		
	Water	Diiodomethane	γ^d	γ^p	γ
Untreated CF	74.39	56.31	23.82	10.64	34.46
POSS coating CF	68.02	51.22	25.40	13.65	39.05
E-51 coating CF	63.21	47.33	26.55	16.08	42.63
E-51+POSS coating CF	55.07	42.02	27.66	20.82	48.48

components. Good wettability between carbon fibers and matrix is closely related to the fiber surface energy, and integrative properties of carbon fiber reinforced resin matrix composites are directly controlled by the wettability of fiber surface and matrix. An excellent wettability means a high interfacial strength and good interface adhesion. Generally, untreated CF has inert surface and poor wettability with resin. Coating treatment can make the fiber surface energy higher or equal to matrix surface energy for improvement of wettability. Surface energy of treated and untreated CF is shown as Table 3.

As shown, after coating treatment, obvious decreasing trends of contact angles were observed from the untreated carbon fibers to the coating treatment fibers. The surface energy of the untreated fibers was 34.46 mJ·m^{-1}, with a dispersion component of 23.82 mJ·m^{-1} and a polar component of 10.64 mJ·m^{-1}. After functionalization, the surface energy obvious increased and its dispersion and polar components of CF-E51-POSS were 27.66 mJ·m^{-1} and 20.82 mJ·m^{-1}, respectively. The surface energy of CF-E51-POSS was 48.48 mJ·m^{-1}. The increased surface energy of the carbon fiber can improve the interfacial adhesion of composites.

Interfacial Properties of the CF/UPR Composites

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 [35].

The interlayers between the CFs and UPR matrix formed by E-51 plus POSS coating were shown in Figure 5. Generally, the different color contrasts in the AFM force modulation images are corresponding to a different modulus. The darker the color is, the higher the modulus [36]. There was not an obvious interphase in Figure 5(A). The fiber and matrix can be observed clearly, the third phase excluding the carbon fibers and UPR resin cannot be found in the image of relative stiffness of untreated CF-UPR. According to the

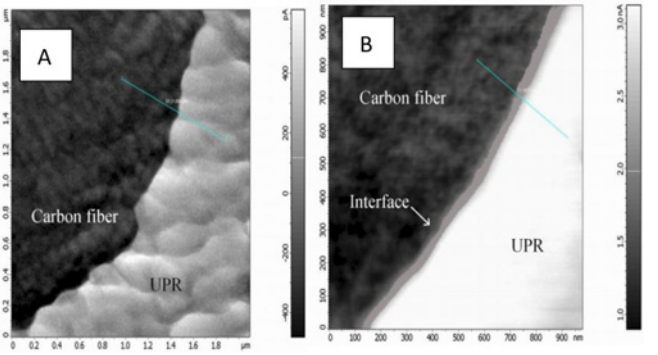

Figure 5. Force modulation AFM images of the composite cross-section; (A) untreated and (B) E-51+Methacryl-POSS coating.

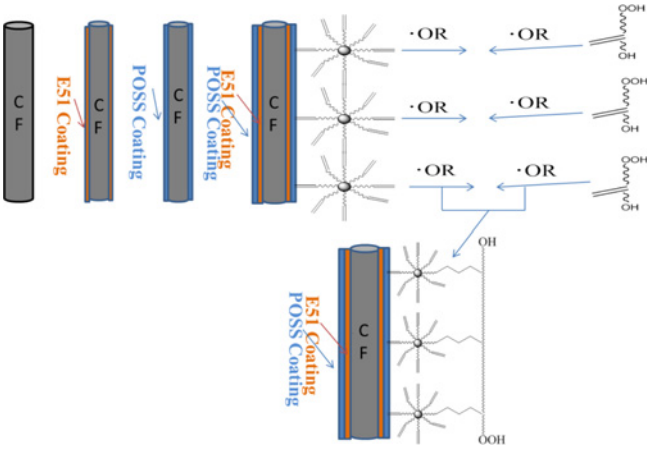

Figure 6. Schematic of interaction mechanism of coating and resin.

similar compatible principle we can know that the inactive and nonpolar surface of carbon fiber and the polar structure of UPR resin result in a rather poor adhesion. Compared with Figure 5(A), there was an obvious interlayer after E51 plus POSS coating in Figure 5(B). That because first we made a thin layer of E51 to stick on the fiber surface, then to coat a layer of POSS on the fiber surface that filled with E51 sizing.

Figure 6 shows the coating and resin interaction mechanism. Owing to excellent adhesion, epoxy is used as common coating to modify the surface of fiber in order to improve the interfacial properties of composites. Unfortunately, there

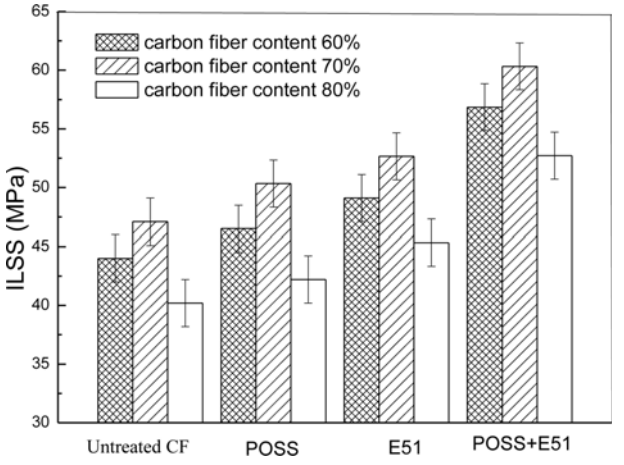

Figure 7. ILSS of composites reinforced by the untreated and modied fibers.

was no reactive group in E51 that can react with UPR in the CF/UPR composites. We introduce the POSS including double bond, which can react with the double bond that in the UPR so that an interlayer can be formed during the curing process. The force modulation image of the hybrid reinforcement reinforced composites (Figure 5(B)) shows obvious contrast among the fiber, interphase and matrix region, revealing a difference in the mechanical properties of these three regions.

Short-beam bending tests were performed to evaluate the interfacial strength of the composites. ILSS of the CF/UPR composites was calculated with equation (3). The results of the experiments are shown in Figure 7, which indicates the effects of different coating. As is shown in Figure 7, the ILSS of the CF/UPR composites had a highest value when carbon fiber content was at 70 %, whatever treated or not.

In theory, high fiber content always means high performance of resulting composites, however, when fiber content reached a certain value, the content of resin is not enough to infiltrate fibers. The phenomenon of lacking glue will cause mechanical performance degradation of resulting composites. The interface is easier to be damaged even when a small force is applied. When the resin content is above a certain target range, insufficient fiber content cannot supply enough interface area, which is not beneficial for improving of interface strength. Finally, then, ILSS of CF/UPR composite will be reduced. Only when the carbon fiber content was within the scope of certain value, the comprehensive performance of composite was optimum. ILSS of the untreated CF/UPR composites was 47.1 MPa, whereas ILSS of the CF with POSS and E51 coating was 50.34 and 52.66 MPa, respectively. ILSS was increased a little, which was only 6.4 % and 10.5 %, respectively. However after E-51 plus POSS coating, ILSS of the composites was increased by 21.9 %. Methacryl-POSS can be used as cure accelerator, which can promote the resin solidification of UPR but Methacryl-POSS has no reaction with the surface of CF due to the inactive surface of CF, so the ILSS was no apparently increased compared to untreated CF. E51 possessed excellent adhesion. It can adhere on the fiber surface very well, however, E51 do not promote the resin solidification of UPR so the ILSS was also no apparently increased compared to untreated CF. In the terms

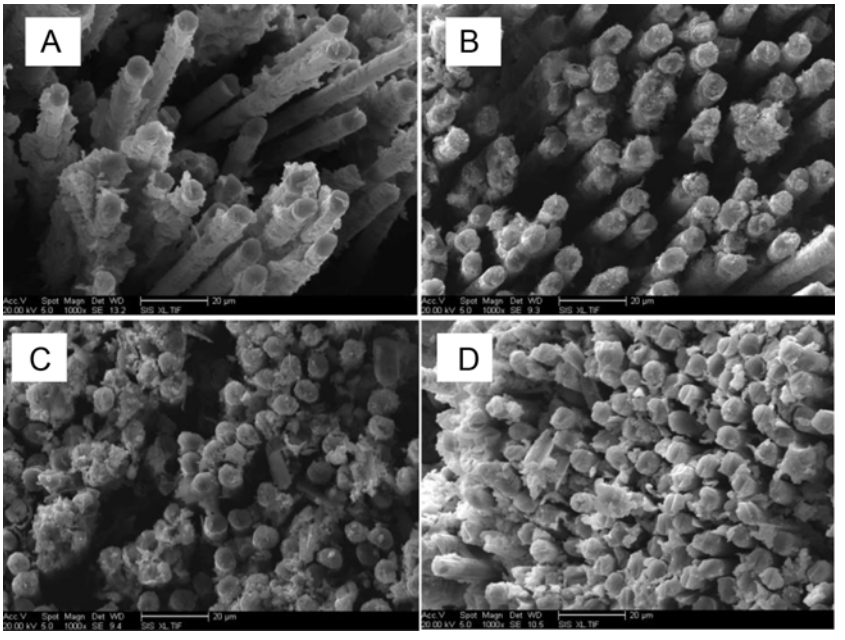

Figure 8. Morphologies of the fractured surface of the carbon fiber composites; (A) untreated, (B) Methacryl-POSS coating, (C) E-51 coating, and (D) E-51+Methacryl-POSS coating.

of E-51 plus POSS system it can combine with the advantages of both and can formed an interlayer so that the ILSS of the CF/UPR composites was significantly improved, that was 60.33 MPa.

SEM observations of the cryo-fractured surfaces of the composites are shown in Figure 8. For the untreated carbon fiber composites, some fibers were pulled out from the matrix, and the interface de-bonding between fibers and matrix was obvious. There was no pulled out fiber after treated with Methacryl-POSS (Figure 8(B)) coating but there was de-bonding between fibers and matrix. This was because that the interaction between fibers and coatings was physical process, however, the interaction between coatings and UPRs was chemical reaction because there were chemical bonds formed by double bonds in coatings during the cure process of UPR. There was also some de-bonding between fibers and matrix as shown in Figure 8(C).

From Figure 8(D), it can be seen that the interfacial adhesion was obviously improved between fibers and matrix and strong interface bonding could be observed. The Methacryl-POSS and E51 had their own advantage. Putting them together as coatings can dramatically improve the interfacial properties of the composites.

Conclusion

Carbon fibers were first coated with a layer of E51, and then coated with a layer of uniform Methacryl-POSS in an attempt to improve the interfacial properties between carbon fibers and UPR. After coating treatment, the ILSS of the composites was increased significantly. The roughness of carbon fiber surface significantly increased after coated with E51 plus Methacryl-POSS. This coating on the fiber surface not only provided a means to enhance the mechanical interlocking with the resin but also provided chemical reaction because there were chemical bonds formed by double bonds in coatings during the cure process of UPR. Before CF leaving the factory, they would be sized by some epoxy compounds to protect the CF and increase the wettability, which the structure was like E51. For CF/UPR composites, manufacturer can coat another layer Methacryl-POSS after E51 sizing to the fiber surface so that the ILSS would be increased. The idea of the method can also be used in other resin systems because the functional groups of POSS are easily changed, for example POSS with epoxy groups can be used in epoxy resin. In order to obtain more increased for ILSS, we will graft Methacryl-POSS and POSS with other functional groups in the CF surface to expect that the interfacial properties can be further improved.

Acknowledgements

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