Materials Letters 64 (2010) 2742–2744

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Improved interfacial properties of carbon fiber/epoxy composites through grafting polyhedral oligomeric silsesquioxane on carbon fiber surface

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A R T I C L E I N F O

Article history:
Received 16 July 2010
Accepted 29 August 2010
Available online 15 September 2010

Keywords:
Carbon fiber
POSS
Surfaces
Composite materials

A B S T R A C T

Carbon fibers were grafted with a layer of uniform octaglycidyldimethylsilyl POSS in an attempt to improve the interfacial properties between carbon fibers and epoxy matrix. Atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and dynamic contact angle analysis were performed to characterize the carbon fibers. AFM results show that the grafting of POSS significantly increased the carbon fiber surface roughness. XPS indicates that oxygen-containing functional groups obviously increased after modification. Dynamic contact angle analysis shows that the surface energy of modified carbon fibers is much higher than that of the untreated ones. Results of the mechanical property tests show that interlaminar shear strength (ILSS) increased from 68.8 to 90.5 MPa and impact toughness simultaneously increased from 2.62 to 3.59 J.

1. Introduction

Carbon fibers are widely used as reinforcements of advanced composites because of their excellent properties, such as high specific strength and modulus, light weight and relative flexibility [1]. However, when applied without previous surface treatment, the physicochemical interaction between carbon fibers and matrix is not strong enough due to their inert and smooth surfaces, which will directly affect the interfacial adhesion of the composites [2]. As a result, extensive research has been devoted to the surface treatment of carbon fibers in order to increase the quantity of surface functional groups and enhance the interactions between fibers and matrix, such as oxidation method [3], electrochemical method [4], plasma treatment [5], and high energy irradiation [6].

Polyhedral oligomeric silsesquioxanes (POSS) are emerging as a new chemical technology for the nano-reinforced organic-inorganic hybrids, which have been applied in diverse areas including aerospace, semiconductor and biological systems, and becoming the focus of many studies due to the simplicity in processing and the excellent comprehensive properties [7]. Although grafting POSS on the carbon fiber surface is a potential modification method, we could not find any reports on this in a literature survey.

Here, we grafted octaglycidyldimethylsilyl POSS on the carbon fiber surface through a series of chemical reactions to enhance the interfacial adhesion between carbon fibers and matrix. The surface chemical composition and morphologies of carbon fibers were investigated by XPS and AFM. Wettability and surface energy of the carbon fibers were obtained by dynamic contact angle analysis. The mechanical properties of composites were evaluated by ILSS and impact toughness.

2. Experimental

PAN-based carbon fibers were purchased from Sinosteel Jilin Carbon Co., China. Octaglycidyldimethylsilyl POSS was purchased from Hybrid Plastics. Thionyl chloride ($SOCl_2$), ethylenediamine (EDA), dimethylformamide (DMF) and tetrahydrofuran (THF) were purchased from Sigma-Aldrich. The carbon fibers were oxidized in a 3:1 (v/v) mixture of concentrated H_2SO_4/HNO_3 at 60 °C for 2 h. Then the carboxyl functionalized carbon fibers were reacted with the mixture solution of 50 ml $SOCl_2$ and 5 ml DMF at 76 °C for 24 h to yield acyl chloride functionalized carbon fibers. Then the fibers were reacted with 50 ml EDA at 80 °C for 24 h. After being washed with deionized water and dried, the amine functionalized carbon fibers were mixed with 0.5 g POSS in 100 ml THF reacting at 50 °C for 6 h to obtain POSS grafted carbon fibers. WSR618 epoxy resin and methyl tetrahyelrophthalic anhydride hardener were supplied by Sinopharm Chemical Reagent Co., used at a mixture ratio of 100:70. The unidirectional prepreg of carbon fibers was put into a mold to manufacture composites. 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. The resin content of the composites was controlled at 35 ± 1.5 mass%, and the width and thickness of specimens were 6.5 and 2 mm. The surface composition analysis was performed on a Scienta ESCA 300 XPS. AFM images were obtained using a NT-MDT Solver P47H system. Dynamic contact angle analysis was performed on a DataPhysics DCAT21 dynamic contact angle meter and tensiometer. Mechanical properties were tested on Instron 5569 universal testing

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doi:10.1016/j.matlet.2010.08.074

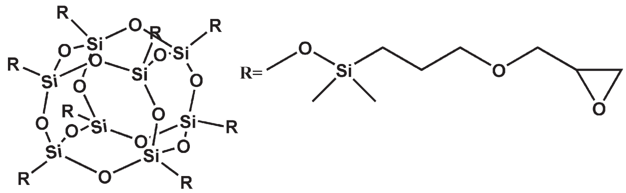

Fig. 1. Structure of octaglycidyldimethylsilyl POSS.

machine and Instron 9250HV drop weight impact test system. The structure of octaglycidyldimethylsilyl POSS is shown in Fig. 1.

3. Results and discussions

The AFM images of untreated, POSS grafted carbon fibers are shown in Fig. 2. Remarkable differences of the surface topography can be observed between the untreated and modified carbon fibers. As shown in Fig. 2a, the surface of 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 modification, a layer of POSS particles are grafted uniformly on the fiber surface and the roughness increases obviously (Fig. 2b). The increased surface roughness can significantly increase the interfacial adhesion by enhancing mechanical interlocking between the fiber and the matrix.

The results of the carbon fiber surface composition obtained by XPS were summarized in Table 1. It is found that the elements of the untreated carbon fiber surface only include carbon, oxygen and insignificant amount of nitrogen. After being grafted with POSS, the carbon content decreased from 84.88% to 66.46% and the oxygen

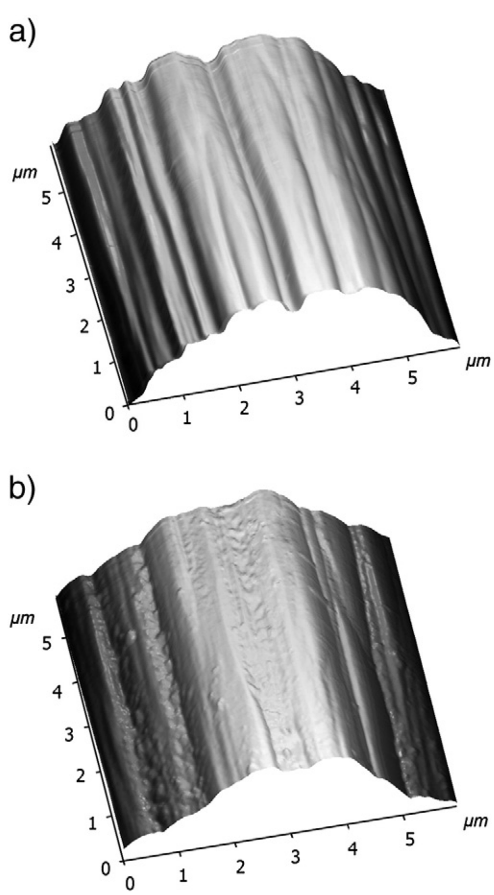

Fig. 2. AFM topography images of carbon fibers. a) untreated, and b) POSS grafted.

Table 1
Surface element analysis of carbon fibers.

Carbon fiber	Element content (%)					O/C	Si/C
	C	O	N	Cl	Si		
As-received	84.88	13.50	1.62	–	–	0.1590	–
POSS grafted	66.46	23.23	1.90	0.10	8.31	0.3495	0.1250

content increased significantly from 13.50% to 23.23%. In addition, significant silicon elements of 8.31% were detected on the fiber surfaces, and surface atomic O/C and Si/C ratios increased sharply, which were due to the Si–O cage structure and the epoxy groups of POSS. These numerous epoxy groups can effectively increase resin compatibility and react with matrix.

The changes of chemical environment and topography of carbon fiber surfaces affect the fiber surface energy as well as its components. In Table 2, the advancing contact angle (θ), the surface energy (γ), its dispersion component (γ^d) and polar component (γ^p) of the untreated and POSS grafted carbon fibers are summarized. As shown in Table 2, the surface energy of untreated fibers was 43 mN m^{-1}, with a dispersion component of 36 mN m^{-1} and a polar component of 7 mN m^{-1}. After modification, obvious decreasing trends of contact angles were observed from the untreated fibers to the POSS modified fibers for both the polar water and the non-polar diiodomethane. The contact angles decreased from 73.21 to 53.68° for water and from 46.85 to 42.52° for diiodomethane. In addition, the surface energy and its components of POSS grafted carbon fibers obviously increased compared with those of the untreated fibers. The increased polar component of modified fibers was due to the epoxy groups of POSS on the fiber surface, and the increased dispersion component was due to the increased roughness caused by POSS particles and the different surface composition of carbon fibers. The increased surface energy can effectively improve the wettability of the fibers by the resin and increase the interfacial strength.

The mechanical property testing results of the composites reinforced by different carbon fibers are shown in Fig. 3. From Fig. 3a, it can be clearly seen that the grafting of POSS significantly increased the interfacial strength of the composites. The ILSS increased from 68.8 to 90.5 MPa by 31.5%. The improvement of the interfacial strength could be attributed to the enhancement of the mechanical interlocking and chemical bonding between the fibers and matrix. After modification, the epoxy groups of POSS play an important role in improving the interfacial adhesion between the fibers and matrix. In addition, the rigid POSS particles grafted on the fiber surfaces can greatly enhance the mechanical interlocking with the resin.

The impact property testing results are shown in Fig. 3b. The initial, propagative and total absorbed energy of untreated carbon fiber composites were 0.45, 2.17 and 2.62 J, respectively. After modification, the impact properties of POSS grafted carbon fiber composites increased. The initial, propagative and total absorbed energy increased to 0.71, 2.89 and 3.59 J, by 57.8%, 33.2% and 37.0%, respectively. When the composites are under load, POSS in the composite interface can induce more cracks which can efficiently absorb the fracture energy, resulting in the increase of the initial absorbed energy. After crack formation, POSS can efficiently change the direction of the crack propagation, which increases the propagative absorbed energy. In a word, the stress concentration around POSS, the inducement of cracks

Table 2
Contact angles and surface energy of carbon fibers.

Carbon fiber	θ_{water} (°)	$\theta_{diiodomethane}$ (°)	γ^d (mN m^{-1})	γ^p (mN m^{-1})	γ (mN m^{-1})
As-received	73.21	46.85	36.00	7.00	43.00
POSS grafted	53.68	42.52	38.32	16.55	54.87

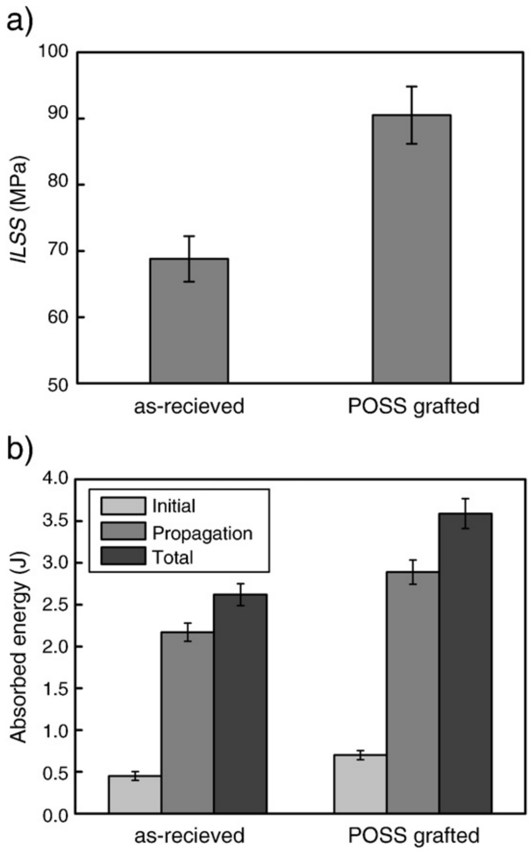

Fig. 3. Mechanical properties of the composites reinforced by untreated and POSS grafted carbon fibers. a) ILSS and b) impact toughness.

and the crack propagation orientation deflection are helpful to improve the impact properties of the composites.

4. Conclusion

Carbon fibers were grafted with a layer of uniform octaglycidyldimethylsilyl POSS in an attempt to improve the interfacial properties between carbon fibers and epoxy matrix. The roughness of carbon fiber surface significantly increased after being grafted with octaglycidyldimethylsilyl POSS. These POSS particles on the fiber surface provided a means to enhance the mechanical interlocking with the resin. XPS results indicate that the oxygen-containing functional groups obviously increased after modification, which is beneficial to increase the chemical bonding between carbon fibers and matrix. The surface energy of the modified fibers is much higher than that of the untreated ones, which can lead to better wettability by the resin and better interfacial adhesion. The mechanical performance tests show that the introduction of octaglycidyldimethylsilyl POSS in the interface region can obviously improve the interfacial strength and simultaneously increase the impact toughness. This significant improvement of mechanical properties is obtained without any effort to optimize the grafting reaction conditions, so it is expected that the interfacial properties can be further increased.

Acknowledgement

The authors gratefully acknowledge financial supports from the Chang Jiang Scholars Program, the National Natural Science Foundation of China (No. 51073047) and the National Natural Science Foundation of China (No. 51003021).

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