

Effects of emulsion sizing with nano-SiO₂ on interfacial properties of carbon fibers/epoxy composites

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Abstract Nano-SiO₂ particles were used to modify epoxy emulsion sizing of carbon fibers to improve the interfacial properties of carbon fibers reinforced epoxy composites. The mechanical interfacial strength between fibers and matrix was investigated by the single fiber fragmentation test and the 3-point short beam shear test, respectively. Dynamic contact angle analysis (DCAA), X-ray photoelectron spectrometry (XPS) and atomic force microscopy (AFM) were performed on the carbon fibers with unmodified sizing and nano-SiO₂ modified sizing. The results indicated that modified sizing with nano-SiO₂ slightly increased the surface energy, the hydroxyl functional group and the surface roughness of carbon fibers compared to unmodified sizing, so that the interfacial shear strength (IFSS) of the single fiber composites and the interlaminar shear strength (ILSS) of composites were enhanced. SEM images of fracture sections of composites proved powerfully that the interfacial adhesion between fibers and matrix was improved after nano-SiO₂ modified emulsion sizing treatment.

Introduction

Carbon fibers are often used as the reinforced material of composites because they exhibit outstanding high tensile strength, high elastic modulus and corrosion resistance properties and so on. For carbon fibers reinforcing composites, the resulting mechanical properties are mainly depending on the particular fiber/matrix system. In addition, the interfaces between fibers and matrix are also stated to be important in improving composites performance, which are to a large extent to transmit stress from the matrix to the fibers [1–7]. In industries, carbon fibers are generally sized or coated with various polymers in order to protect the fibers and make handling easier after surface oxidation treatment. Remarkably, people find that sizing also plays an important role in improving the interfacial adhesion between fibers and matrix [8–13]. Sizings for carbon fibers are commonly classified into the solution type and the emulsion type. From the standpoints of economy, safety and hygiene, emulsion type sizing is ordinarily used. It has been reported that the sizing layer as the additional phase can improve mechanical interlocking by increasing the fibers surface roughness [9, 13]. Furthermore, sizing can be dissolved into the matrix, resulting in the chemical interactions of the matrix resin with the surface of sized fibers [14].

Recently, nanoparticles such as nano-SiO₂, nano-Al₂O₃ and nano-TiO₂ etc., modifying the mechanical interfacial properties of composites, have been reviewed by many literatures [15–19]. Based on significant effects of sizing on the interfacial properties of composites, we further selected inorganic nano-SiO₂ to modify emulsion sizing of carbon fibers so as to increase the interfacial adhesion degree of carbon fibers/epoxy composites. In this paper, the mechanical interfacial properties of the composites were

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studied by the single fiber fragmentation and the short beam shear tests. DCCA, XPS and AFM were used to investigate the surface physical and chemical changes of carbon fibers with unmodified emulsion sizing and nano-SiO₂ modified emulsion sizing.

Experimental

Materials

The epoxy resin (*N, N, N', N'*-teraglycidyl-4, 4'-diaminodiphenyl-methane, trade name: AG-80) was supplied by Shanghai synthesized resin institute (China). The diglycidyl ether of bisphenol-A epoxy (trade name: E-51) was obtained from Tianjin epoxy factory (China). Curing agent 4,4'-diaminodiphenyl sulfone (trade name: DDS) and triethylenetetramine were obtained from Sinopharm Group Chemical Reagent Co. Ltd (China) and Shanghai Chemical Reagent Co.(China), respectively. The emulsifiers were the emulsifier mixtures prepared in our laboratory. Coupling agent (γ -(Methylacryloxy) propyltrimethoxyl silane, trade name: KH-570) is manufactured by Nanjin Shuguang Chemical factory (China). Nano-SiO₂ with the particle size of 15–25 nm was purchased from Zhoushan Mingri Nanomaterial Co. Ltd (China). Polyacrylonitrile (PAN)-based carbon fibers used were produced in our laboratory. Its average diameter was 7 μ m. The tensile strength and elastic modulus were 3.53 and 210 GPa, respectively.

Preparation of emulsion sizing

Nano-SiO₂ particles were pretreated by silane coupling agent and then added to acetone solution of epoxy resin AG-80 at different ratios. The ultrasonic waves and a high-speed homogenizer were used to make nanoparticles homogeneously disperse in the epoxy solution. In the following, acetone in the solution was absolutely volatilized at 80 °C. The appropriate amount of emulsifiers was blended with epoxy resin in the heating condition with 80 °C. Then deionized water was added slowly, and the emulsification was carried out with acutely stirring at ambient temperature. As a result, emulsion sizings with the different ratio of nano-SiO₂ to sizing epoxy were prepared.

Sizing treatment of carbon fibers

Carbon fibers tows were pulled off a spool at a speed. The fibers were placed under tension by a nip roller and then passed through sizing with the concentration of 1 wt.%. Carbon fibers containing emulsion sizing were dried immediately in a hot gas oven.

Single fiber fragmentation test

A single fiber was embedded along the centerline of a silicon rubber mold with dog-bone shaped cavity. Epoxy resin E-51 containing 10 wt.% triethylenetetramine was degassed under vacuum and carefully poured into the cavity. The resin was cured at 80 °C for 2 h and post-cured at 125 °C for 1 h and then the specimens were removed from mold and stored in desiccator.

The single fiber composites samples were pulled in tension with 5% specimen strain at a speed of 1 mm/min. The pulling was stopped when the fiber fragmentation reached saturation. The fragments length values were measured using an optical microscope.

According to Kelley–Tyson theories [20, 21], the interfacial shear strength (IFSS) was calculated using the following equation:

$$\tau = \sigma_c d / 2L_c,$$

where d is the fiber diameter, and σ_c is the fiber tensile strength at L_c , the critical length of fragments.

Short beam shear test

Carbon fibers were impregnated using an acetone solution of epoxy resin AG-80 with 10 wt.% DDS for manufacturing prepregs. The composites laminates were cured with 10 plies prepregs using a vacuum thermal-compressed molding method, which were vacuumized at room temperature and cured for 30 min at 150 °C and 120 min at 200 °C at a press of 7 MPa.

The interlaminar shear strength (ILSS) of the resulting composites was conducted by the 3-point short-beam shear test, according to the ASTM D-2344 standards. A total of 10 data points were collected, and then averaged.

Characterizations

The fracture sections of composites via the short-beam shear test were observed by JEOL JSM-6360LV model scanning electron microscope (SEM). The two liquids dynamic contact angles of carbon fibers were measured by a Cahn DCA322 model dynamic contact angle analyzer. The properties of two probe liquids are listed in Table 1. The surface chemical analysis of carbon fibers were carried out using an ESCALab220i-XL photoelectron spectrometer from VG Scientific using 300W Al K_{α} radiation. The base pressure was about 3×10^{-9} mbar. The surface roughness measurements were performed with a Nanoscope IIIa atom force microscopy (AFM) from Digital Instrument Co.

Table 1 Surface energy components of two probe liquids

Surface energy (mJ/m ²)	γ_L^T	γ_L^d	γ_L^p
Water	72.8	29.1	43.7
Glycerol	64.0	34.0	30.0

Results and discussion

Effects of sizing treatment on the mechanical interfacial properties of composites

Figure 1 shows the ILSS and IFSS test results of composites, which indicate that the interfacial adhesion strengths between fibers and matrix are increased after nano-SiO₂ modified sizing treatment. This may be the result that for the fiber surface with modified sizing, the surface characteristics of carbon fibers are changed with increasing of the amount of nano-SiO₂ with high surface areas and many active functional groups. In other words, the wettability of the matrix by carbon fibers and the surface roughness of carbon fibers are further enhanced. Generally, the chemical interactions between fibers and matrix have an important effect on the mechanical properties of composites. When carbon fibers are sized by emulsion with nano-SiO₂, there is a possible increasing trend in the chemical interactions of the interface. In addition, nano-SiO₂ can act as stress concentrators at interfaces to improve the mechanical interfacial strength, which assist in holding back excessive stress spreading in the flaw and changing the crack propagation paths. It can be seen from Fig. 1c that there are the maximal IFSS and ILSS values for carbon fibers/epoxy composites at the

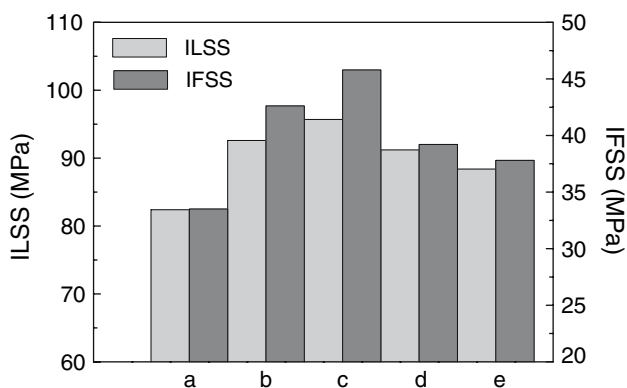


Fig. 1 The IFSS of single fiber composites and the ILSS of composites: (a) sized with unmodified sizing; (b) sized with modified sizing at 0.5 wt.% ratio of nano-SiO₂ to sizing epoxy; (c) sized with modified sizing at 1.0 wt.% ratio of nano-SiO₂ to sizing epoxy; (d) sized with modified sizing at 2.0 wt.% ratio of nano-SiO₂ to sizing epoxy; (e) sized with modified sizing at 3.0 wt.% ratio of nano-SiO₂ to sizing epoxy

1 wt.% ratio of nano-SiO₂ to sizing epoxy. When the nano-SiO₂ content is much than 1 wt.% as in Fig. 1d, e, the ILSS and IFSS values decreased slightly, which may be resulted from the agglomeration of nanoparticles.

The fracture sections topographies of composites are shown in Fig. 2 by SEM. As seen in Fig. 2a, there are some carbon fibers pulling out and holes on the fracture section of the composites with unmodified emulsion sizing. The fibers debonding happened at interfaces between fibers and matrix. After modified sizing treatment, the compact fracture sections of composites are observed in Fig. 2b, evidently showing the anti-shear phenomena.

Surface energy measurements

Table 2 shows the surface contact angles and surface energy compositions for the carbon fibers with unmodified sizing and modified sizing. The contact angles of carbon fibers with nano-SiO₂ modified sizing are lower than that of the fibers with unmodified sizing. It can be concluded that new active sites on the carbon fiber surface are obtained after modified sizing treatment, leading to the increase of polar functional groups. The similar results are also found that the total surface energy and the polar component of surface energy for the carbon fibers with modified sizing are increased by 23.6 and 29.7%, respectively, compared to that with unmodified sizing. However, there is not distinct change for the dispersive component of the total surface energy. With the increase of surface polar energy, the wettability of the matrix by carbon fibers is also improved, leading to increasing the interfacial adhesion properties between fibers and matrix.

XPS analysis

The surface atomic compositions of the carbon fibers with unmodified sizing and nano-SiO₂ modified sizing are given in Table 3. When the ratio of nano-SiO₂ to sizing epoxy is 1.0 wt.% for modified sizing, the oxygen content of the fiber surface with modified sizing is 19.3% higher than that of the fibers with unmodified sizing. In addition, the silicon content is also increased about twice that of the carbon fibers with unmodified sizing.

Figure 3 shows C1s peaks of XPS spectra of the carbon fibers with unmodified sizing and modified sizing. The relevant percentages of functional groups (–C–C, –C–OH, –C=O; –COOH) are estimated from these curve fit C1s photopeaks and are listed in Table 4. It is found that the percent content of –C–C bond, carbonyl groups (–C=O) and carboxyl groups (–COOH) do not change significantly after and before nano-SiO₂ modified sizing treatment. Surprisingly, the percent content of hydroxyl groups

Fig. 2 SEM images of fracture sections of composites: (a) sized with unmodified sizing; (b) sized with modified sizing at 1.0 wt.% ratio of nano-SiO₂ to sizing epoxy

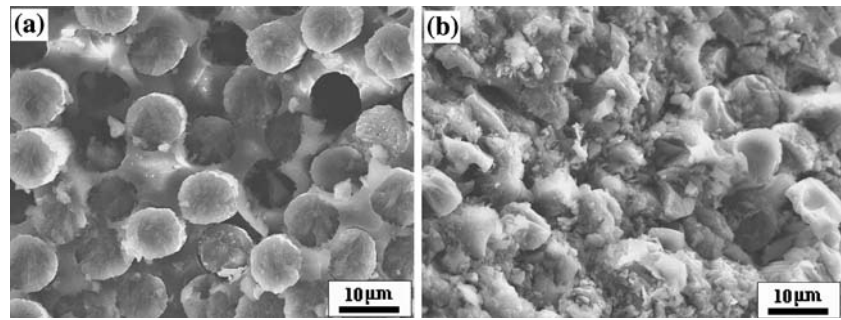


Table 2 Surface properties of carbon fibers with unmodified sizing and modified sizing at 1.0 wt.% ratio of nano-SiO₂ to sizing epoxy

Carbon fiber	Contact angle (θ)		Surface energy (mJ/m ²)		
	Water	Glycerol	γ_S^T	γ_S^d	γ_S^p
Unmodified sized	57.7	54.5	44.4	10.0	34.4
Modified sized	43.7	43.3	54.9	10.3	44.6

Table 3 XPS surface compositions of carbon fibers with unmodified sizing and modified sizing at 1.0 wt.% ratio of nano-SiO₂ to sizing epoxy

Carbon fiber		Photopeaks					
		C1s	O1s	N1s	Cl2p	S2p	Si2p
Unmodified sized	B.E. (eV)	284.7	532.3	399.2	199.9	168.0	102.6
	A.C. (%)	82.5	13.5	2.2	0.2	0.2	1.4
Modified sized	B.E. (eV)	284.6	532.4	400.0	199.8	167.7	102.6
	A.C. (%)	78.2	16.1	1.9	0.6	0.2	3.0

Fig. 3 C1s XPS spectra of carbon fibers: (a) sized with unmodified sizing; (b) sized with modified sizing at 1.0 wt.% ratio of nano-SiO₂ to sizing epoxy

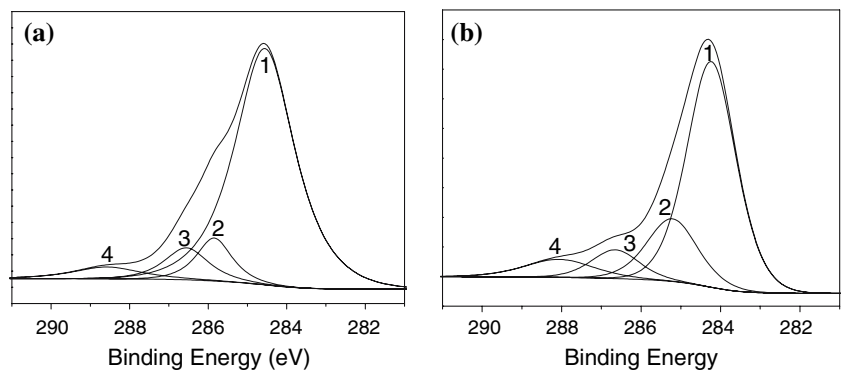


Table 4 XPS carbon 1s curve fit results of carbon fibers with unmodified sizing and modified sizing at 1.0 wt.% ratio of nano-SiO₂ to sizing epoxy

Carbon fiber		C1s Photopeak			
		1	2	3	4
Unmodified sized	B.E. (eV)	284.2	285.5	286.4	288.6
	P.C. (%)	79.2	8.5	7.8	4.5
Modified sized	B.E. (eV)	284.4	285.6	286.5	288.0
	P.C. (%)	77.9	12.1	5.3	4.7
Peak assignment		-C-C	-C-OH	-C=O	-COOH

(–C–OH) of the fiber surface is remarkable increased after nano-SiO₂ modified sizing treatment. The increase of hydroxyl groups on the fiber surface is in favor of improving the chemical interactions between fibers and matrix.

Surface topography

Figure 4a, b show the AFM images of the carbon fibers surface with unmodified sizing and nano-SiO₂ modified sizing, respectively. Compared to unmodified sizing, sizing with nano-SiO₂ further changes the surface topography at the nanometer lever. As seen in Fig. 4a, the fiber surface with unmodified sizing exhibits clearly ridges running in the fiber direction. After modified sizing treatment, there are some concave and convex hills on the fiber surface, showing a significant increase in roughening compared to the fiber with unmodified sizing. Table 5 summarizes the results of roughness analysis of the carbon fibers surface after and before nano-SiO₂ modified sizing treatment from AFM images. The results indicate that the typically mean surface roughness (R_a) is 5.1 nm for the carbon fibers with unmodified sizing, whereas the value of R_a for the carbon

Table 5 Surface roughness of carbon fibers with unmodified sizing and modified sizing at 1.0 wt.% ratio of nano-SiO₂ to sizing epoxy

Carbon fibers	Unmodified sized	Modified sized
Root mean square roughness (RMS)	6.9 nm	10.8 nm
Mean roughness (R_a)	5.1 nm	8.5 nm
Maximum height (R_{max})	88.5 nm	106.8 nm
Dimensions	1 $\mu\text{m} \times 1 \mu\text{m}$	1 $\mu\text{m} \times 1 \mu\text{m}$

fibers with modified sizing is 8.5 nm, possessing the 66.7% increment. This change in surface topography is presumable due to the variations in the thickness of sizing. The differences of thickness may be resulting from the effect of nano-SiO₂. The increase of the fibers surface roughness could lead to the intimate interfacial adhesion between fibers and matrix by mechanical interlocking.

Conclusions

The IFSS of single fiber composites and the ILSS of composites are increased after nano-SiO₂ modified sizing treatment. When the ratio of nano-SiO₂ to sizing epoxy is 1.0 wt.%, there are the maximal IFSS and ILSS values. SEM images show the fracture section of composites with modified sizing is more compact and the fiber debonding is more difficult than that with unmodified sizing. The hydroxyl groups and surface polar energy on the carbon fibers surface with modified sizing are clearly increased. From AFM analysis, it can be seen that modified sizing changed the surface roughness values on a microscopy scale. As a result, nano-SiO₂ modified epoxy emulsion sizing for carbon fibers further improves the chemical and physical properties of the fiber surface, resulting in the increase of the mechanical interfacial properties of the composites.

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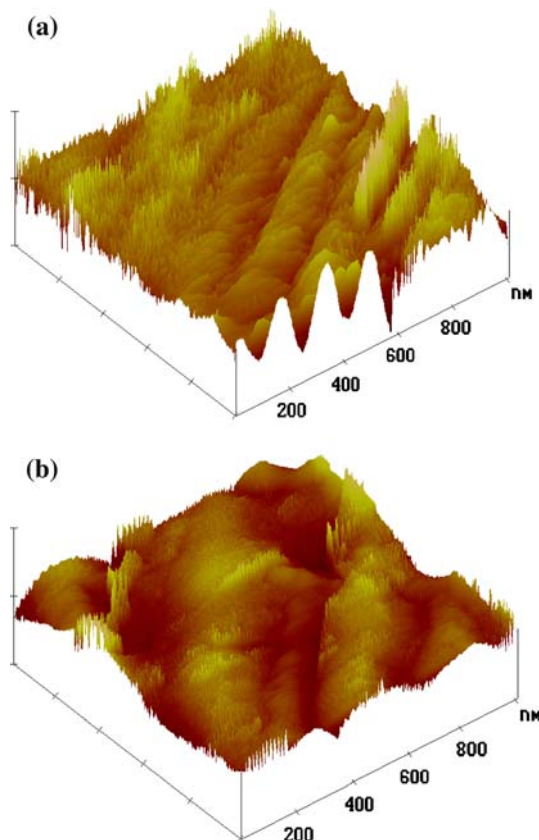


Fig. 4 AFM images of carbon fibers surface: (a) sized with unmodified sizing; (b) sized with modified sizing at 1.0 wt.% ratio of nano-SiO₂ to sizing epoxy

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