



Property Analysis of Carbon Fiber with Vinyl Ester Resin Type Sizing Agent

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The influences of vinyl ester resin type sizing agent on the properties of carbon fiber and composite were studied. The yarn abrader, X-ray photoelectron spectroscopy were used to characterize wear resistance and chemical element of carbon fiber. Interlaminar shear strength of composite was tested by universal testing machine. The results indicated that wear resistance of sized carbon fiber was significantly improved. X-Ray photoelectron spectroscopy results demonstrated that the activated function groups of sized carbon fiber were more than desized one. The interfacial adhesion of sized carbon fiber/vinyl ester resin (CF/VE) composite was strengthened and interlaminar shear strength of sized carbon fiber/vinyl ester resin composite reached 45.9 MPa.

Key Words: Sizing agent, Carbon fiber, Vinyl ester resin.

INTRODUCTION

Carbon fibers (CFs) are widely used as reinforcements in composites, especially in advanced composites¹⁻⁴. Mechanical properties of composites not only depend on the fiber and matrix properties but also the fiber/matrix interface. Strong interface can transfer the load efficiently from the matrix to the fiber, resulting in stronger composites¹. Consequently, various methods are used to modify the surface of carbon fibers to improve the adhesion of carbon fibers/matrix, such as surface treatment and sizing⁵. It is reported that the purpose of sizing is to insert a polymer film between the carbon fiber and the resin matrix to control the properties of fiber/matrix adhesion⁶. The sizing can also improve the handle ability of carbon fiber which includes fiber protection, fiber alignment and fiber wettability^{7,8}. To work best, sizing agent must match with the matrix. The objective of this study is to prepare low cost vinyl ester resin type sizing agent to satisfy the application of carbon fiber reinforced vinyl ester resin composites. The vinyl ester resin type sizing agent was prepared and the effects of sizing on carbon fiber and composites were experimentally characterized, including wear resistance, surface chemical elements and interfacial adhesion property.

EXPERIMENTAL

Raw material: Commercially available polyacrylonitrile-based carbon fiber T300, 3 k, the average diameter of fibers is 7 μm , the density is 1.78 g/cm^3 , was produced by Jilin Chemical

Industrial Company, China. The fibers were refluxed in boiling acetone for 36 h using a Soxhlet apparatus to remove the sizing agent coated on fibers. Vinyl ester resin V-3201, viscosity of 0.3-0.5 Pa·s, styrene content of 30 %, molecular weight about 400, which was supplied by Shandong Yisheng Resin Factory, China. The butadiene-acrylonitrile oligomer (ETBN), molecular weight between 3000 and 4000, viscosity of 500 Pa·s at 25 °C, was supplied by Beijing Devote Chemical Company, China. Polyoxyethylene nonylphenol phosphoric ammonium (NP-10A) was homemade using chemical precursor NP-10P. Polyoxyethylene castor oil (EL-20) was obtained from Venture Grease Chemical Plant, China.

Preparation of sizing agent and sized carbon fiber: The sizing agent was prepared by phase inversion emulsification method. The emulsifiers were mixed into the acetone solution of butadiene-acrylonitrile oligomer modified vinyl ester resin. Other assistants such as silane coupling agent and penetrant were also added. The mixture was dispersed in deionized water homogeneously using FA25 Lab Hishear Disperser under a constant stirring rate. An emulsion with 30 wt.% solid component was obtained.

The sizing agent with 0.5 wt. % solid component was obtained with deionized water. Dipping method was used in sizing process. The carbon fibers was immersed in the sizing agent at proper rate by use of a dip tank in conjunction with automatic processing equipment for continuous running the carbon fibers through the dip tank. Then the carbon fibers was dried at 100 °C for 20 min.

Preparation of carbon fiber/vinyl ester resin composites: Vacuum bag molding technology was used in the preparation of carbon fiber/vinyl ester resin composites. The vinyl ester resin/methyl ethyl ketone peroxide/cobaltous naphthenate was mixed uniformly with weight ratio of 100:2:2. Then a vacuum was drawn on the bag formed by the film and the resin was infused. The specimens were cured at room temperature for 3 h and postcured at 100 °C for 1 h for vinyl ester resin.

Characterization

Wear resistance of carbon fibers: Wear resistance of carbon fiber was tested by yarn abrader (LFY-109A type, Shandong Textile Scientific Research Institute Instruments Research Institute, China). There was a rotary grinding roll cylinder on yarn abrader. The abrasive paper was wrapped on the surface of cylinder. The stretched fiber with certain tension under constant pressure was straddled on the abrasive paper. Five carbon fiber bundles were measured and the average wear resistance times were recorded. The 240-# abrasive paper was used in this paper.

X-ray photoelectron spectroscopy: The surfaces of desized and sized carbon fibers were evaluated using X-ray photoelectron spectrometer (K-Alpha type, Thermofisher Company, America) and monochromatic AlK_{α} radiation (1486.6 eV). A spot of 200 μ m in diameter, 200 eV of pass energy for survey scan and 50 eV for high resolution scan were used in all the measurements.

Interlaminar shear strength: According to the ASTM D2344, short-beam-shear test of the unidirectional composites was carried out on a universal testing machine (WDW-30 type, Shanghai Shenli Testing Machine Company, China) at a span-to-depth ratio of 6/1. More than six composite specimens of 60 % volume content of carbon fibers with dimensions of 20 mm \times 6 mm \times 2 mm were selected for each interlaminar shear strength test. Interlaminar shear strength value for the short beam test was calculated according to eqn. 1³:

$$\text{Interlaminar shear strength} = 3 P_b / (4bh) \quad (1)$$

where P_b is the maximum compression load at fracture, N; b is width of specimen, mm; h is thickness of specimen, mm. Each reported interlaminar shear strength value of composites was the average of results from measurement of six specimens.

The fracture surfaces of interlaminar shear strength samples were examined by scanning electron microscopy (HITACHIS-2500 type, Hitachi Company, Japan).

RESULTS AND DISCUSSION

Wear resistance analysis: It can be seen from Table-1, wear resistance times of sized and desized carbon fibers are 1368 and 567, respectively, which indicates the wear resistance of carbon fibers are greatly improved after sizing treatment. The untreated carbon fiber is brittle and of poor wear resistance. The sizing agent plays the role of protecting the fiber from the fluffs and fiber breakage^{9,10}. So the workability of carbon fibers is also significantly modified during the subsequent processing such as woven of carbon fiber fabric. The strand integrity of carbon fiber will also be improved through sizing film attached firmly on the fiber surface.

TABLE-1
WEAR RESISTANCE OF CARBON FIBERS

Carbon fibers	Wear resistance times
Desized	567 \pm 59
Sized	1368 \pm 95

X-ray photoelectron spectroscopy analysis: The surface composition of desized and sized carbon fibers was detected by XPS and the results are given Fig. 1. The values of the binding energy (B.E.) and the per cent concentration (P.C.) of each curve fit photopeaks of carbon fibers are listed in Table-2.

TABLE-2
CHANGES OF ELEMENT AMOUNT ON THE SURFACE OF DESIZED AND SIZED CARBON FIBERS

Type		Photo peaks		
		C1s	O1s	Si2p
Desized carbon fiber	B.E. (eV)	285.46	533.20	–
	P.C. (%)	86.83	13.17	–
	O.C (%)	15.17	15.17	15.17
Sized carbon fiber	B.E. (eV)	293.08	540.58	106.58
	P.C. (%)	72.28	19.73	7.99
	O.C (%)	27.30	27.30	27.30

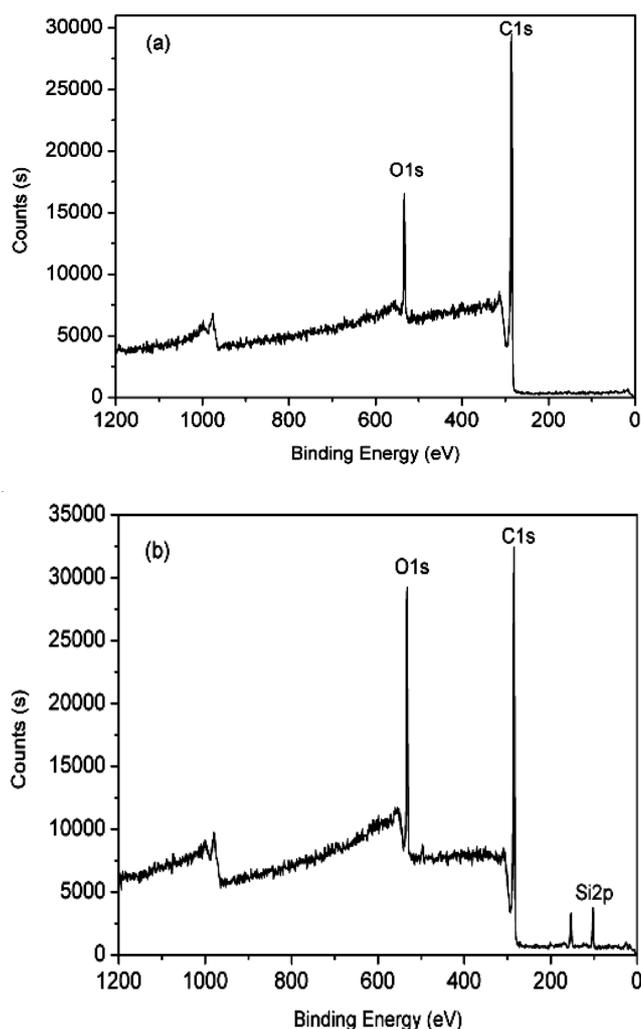


Fig. 1. XPS spectra of the carbon fiber: (a) desized, (b) sized

It can be seen that the main elements on the surfaces of carbon fiber are carbon (C), oxygen (O) and silicon (Si). The C per cent concentration on surface of carbon fiber decrease and the O per cent concentration increase after sizing treatment. The per cent concentration ratio of O to C for carbon fiber shows gains of 12.13 % after sizing treatment. The presence of Si on the surface of sized carbon fiber may attribute to silane coupling agent in the sizing agent. Surface functional groups of the carbon fibers are considered to be critical properties in predicting the adhesion between fibers and matrix. The results indicate that the activated oxygen function groups on the surface of carbon fiber increase. So the strong interfacial adhesion between sized carbon fiber and suitable resin matrix can be formed by activated oxygen function groups on the surface of sized fibers.

Interlaminar shear strength analysis: Interfacial adhesion property between carbon fiber and matrix has a significant influence on mechanical properties of composites. Sizing layer as the additional phase affects the mechanical properties of composites¹. Interlaminar shear strength values of desized and sized carbon fiber/vinyl ester resin (CF/VE) composites are shown in Fig. 2.

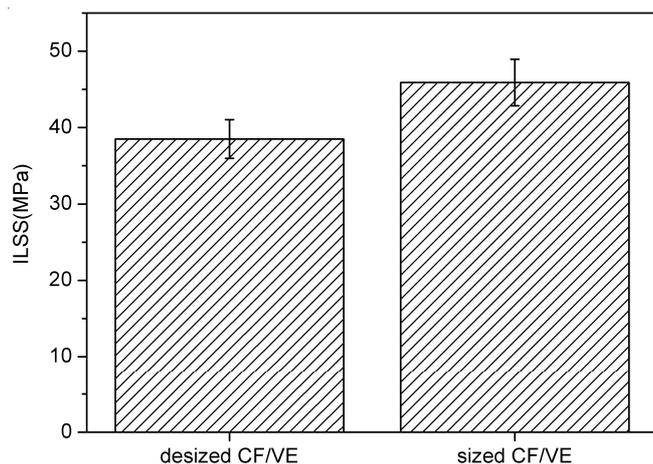


Fig. 2. Interlaminar shear strength values of desized and sized carbon fiber/vinyl ester resin composites

Fig. 2 indicates that interlaminar shear strength value of sized carbon fiber/vinyl ester resin composite reaches 45.9 MPa, increasing by 19.2 %, compared with desized carbon fiber/vinyl ester resin composite (38.5 MPa). The sizing agent acts as intermediate layer to transfer the load efficiently from vinyl ester resin matrix to the carbon fiber and avoid stress concentration, resulting in high interlaminar shear strength of sized carbon fiber/vinyl ester resin composite. The poor interfacial adhesion between vinyl ester resin matrix and desized carbon fiber is due to flaws, fluffs and breakage of desized carbon fiber and poor wetting property between fiber and matrix resin.

SEM images of the fracture surface of carbon fiber/vinyl ester resin composite were shown in Fig. 3. It can be seen from Fig. 3(a), some carbon fibers are pulled out from vinyl ester resin matrix, which illustrates the weak layers in the fiber/resin interface region. Strong interlocking of fiber/matrix could be observed in Fig. 3(b), a large amount of resin matrix is

covered on fibers surface, which indicates strong interfacial adhesion between sized carbon fibers and vinyl ester resin matrix. The results verify that the presence of the sizing agent on carbon fiber surface is positive for the interfacial adhesion.

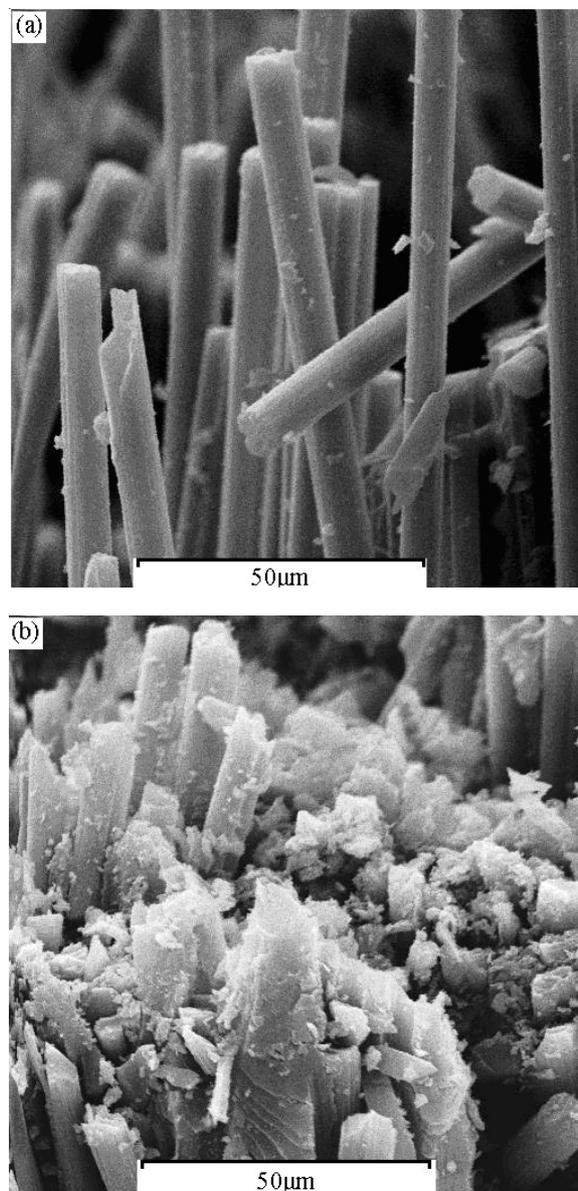


Fig. 3. SEM images of the fracture surface: (a) desized carbon fiber/vinyl ester resin composite, (b) sized carbon fiber/vinyl ester resin composite

Conclusion

The influences of vinyl ester resin type sizing agent on the properties of carbon fiber and composite were studied. The results indicated the handling characteristics of sized carbon fiber could be significantly improved due to the increase of wear resistance. XPS results demonstrated that the activated function group of sized carbon fiber was more than desized one. The strong interfacial adhesion between sized carbon fiber and suitable resin matrix would be formed by activated oxygen function groups on the surface of sized fibers. The interfacial adhesion of sized carbon fiber/vinyl ester resin composite was strengthened and interlaminar shear

strength of sized carbon fiber/vinyl ester resin composite reached 45.9 MPa, which increased by 19.2% compared to desized carbon fiber/vinyl ester resin composite.

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