Effect of the Concentration of the Sizing Agent on the Carbon Fibers Surface and Interface Properties of Its Composites

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ABSTRACT: The effect of the concentration of the sizing agent on performances of carbon fiber and carbon fiber composites has been investigated. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) were applied to characterize carbon fiber surface topographies. At the same time, the single fiber strengths and Weibull distribution were also studied. The interlaminar shear strength and hygrothermal ageing test have been used to study the effect of fiber coatings on the interface of the composites. The analysis of the results shows that the sizing level is essential for improving the surface of carbon fibers and its composite performance. Different concentrations of the sizing agent have different contributions to the wetting performance of carbon fibers. Among the three concentrations of sizing agent studied (1 wt %, 1.5 wt %, and 2 wt %), the optimal sizing level is 1.5 wt %. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 125: 425–432, 2012

Key words: adhesion; coatings; mechanical properties; fibers; surfaces

INTRODUCTION

Carbon fibers are lightweight and have particularly superior properties with respect to specific strength, specific modulus, superior heat resistance, and chemical resistance. They are particularly effective as reinforcing fibers of fiber-reinforced composite and are used for a wide range of applications during the last two decades.[1–3]

In order to obtain carbon fibers with adequate convergence and superior processability, such as weaving process and other molding processes of the carbon fiber, a sizing agent is introduced to the system. The sizing on carbon fibers has been reported to serve in several aspects: improves in handle ability of the carbon fibers yarn in processing, protects the carbon fibers surface, and enhances the interfacial properties.[4–8]

However, the amount of sizing agent must be strictly controlled in order to provide satisfactory processability and other workabilities for the resulting carbon fiber bundles. The influence of the selected concentration of the sizing agent on the carbon fiber and its composites are different. The high concentration of the sizing agent makes its capacity of adsorbing moisture in the air enhanced due to the presence of hydrophilic groups in its molecules. It can make the processability and other workabilities of the carbon fibers decreased when formed into fabrics. On the other hand, the low concentration of the sizing agent leads to the weak converging performance. So the sizing agent plays key role in the bonding. At present, however, since the sizing agent is the trade secret, there are no convincing works published reporting the concentration range of the sizing agent.

The aim of the present work was to study the influence of the concentration of the sizing agent on the properties of carbon fibers and to investigate the nature of the external fiber surface and the materials themselves. In order to obtain carbon fibers with adequate convergence required for forming stable carbon fibers with superior processability and other workability when forming into fabrics. Three concentration of the sizing agent (1 wt %, 1.5 wt %, and 2 wt %) was studied. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used to characterize carbon fiber surface topographies and failure surfaces. The interlaminar shear

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strength, hygrothermal ageing, single fiber strengths, and Weibull distributions have been used to study the effect of fibers coatings on the adhesion of surface.

EXPERIMENTAL

Materials

The unsized carbon fiber, 3k, whose average diameter is 7 μm, the density 1.78 g/cm^3, the linear density 0.199–0.202 g/m, which was supplied by Jilin Chemical Industrial Bloc. The sizing agent HIT has been prepared in the lab.[9] The sizing agents C_1, C_2, and C_3 corresponded to three concentrations of sizing agent 1 wt %, 1.5 wt %, and 2 wt %, respectively. The coating time was 20 s. The matrix system used was Epoxy 618 and the harder was H-256, which were both supplied by vicinal market.

Characterization

Surface topography

The morphological changes on the surface of carbon fibers subject to different sizing agent concentrations were examined by AFM. AFM observations were carried out in non-contact mode by Solver P47 atomic force microscope made in Russia NTMDT Corporation. A single carbon fiber was fastened to a steel sample mount using double sided tape. All images were collected in air using the tapping mode with a silicon nitride probe. The scanning scope was 4 × 4 μm and the scan rate was 1.85 Hz.

SEM studies the surfaces of sized carbon fibers and failure surfaces of the composites using the FEI Sirion 200 scanning electron microscope (Royal Dutch Philips Electronics Ltd., Netherlands). For SEM tests, samples were coated with Au for several nanometers thick.

Wettability testing

Wettability testing was carried by the electronic analytical balance ALC-110.4 (Shanghai Cany Precision Instrument Co., Ltd). The wettability testings were started after the prepared samples had been suspended over the framework till it got to balance. The infiltration time was about 90 min. At first the data were taken every 1 s, then every 3 s and at last every 30 s.

The single fiber strengths and Weibull distributions

The fibers were glued to paper strips at both ends using glue adhesive, loaded and evaluated according to the standard ASTM-D3379 using an electronic universal tensile strength testing machine at a crosshead speed of 5 mm/min. A total of 40–50 data points were collected for each fiber type. The paper strips were then cut off before the test.

Interlaminar shear strength of carbon fibers/epoxy composites

The resin/hardener mixture was thoroughly stirred for 15 min with the ratio 100 : 32. The ILSS of carbon fiber/Epoxy (CF/EP) was determined according to ASTM D2344, with a crosshead speed 2 mm/min. The values of ILSS were calculated by the following eq. (1):

$$\mathrm{ILSS} = \frac{3P_b}{4bh} \tag{1}$$

Hygrothermal ageing

The ILSS was measured after the specimen being boiled in the 100°C water for 48 h.

RESULTS AND DISCUSSION

Surface topography

The interfacial behavior depends to a great extent on the carbon fiber surface.[10] The surface topographies of sized carbon fibers with different concentrations sizing agent were observed by AFM. The concentration of the sizing agent appeared to greatly affect the external fiber surface, and the results are shown in Figure 1. The results demonstrated that there were a number of longitudinal streaks dispersing on the carbon fibers surface, but the depths of the longitudinal streaks on the surface were different. The longitudinal streaks in the C_3 sized carbon fibers almost disappeared in Figure 1(c). The shallow longitudinal streaks dispersed on the C_2 sized carbon fibers in the Figure 1(b), while the deep and uneven longitudinal streaks appeared in the C_1 sized carbon fibers [Fig. 1(a)].

Figure 2 shows the SEM images of sized carbon fibers with different concentrations sizing agent, respectively. Remarkable differences of the surface topography can be observed among the sized carbon fibers. Figure 2(a,b) show a micrograph of C_1 sized carbon fibers, indicating that there were a number of longitudinal streaks clearly on it. However, the holes were clear observed on the carbon fibers being treated with C_1 sizing agent [Fig. 2(b). Compared with the C_1 sizing agent sized carbon fiber, changes of the surface topography were observed for the carbon fibers being treated with C_2 sizing agent [Fig. 2(c,d)]. It was found that C_2 sizing agent distributes uniformly on the fiber surface and the grooves become even. The grooves on the surface of C_3 sized carbon fibers almost disappear in

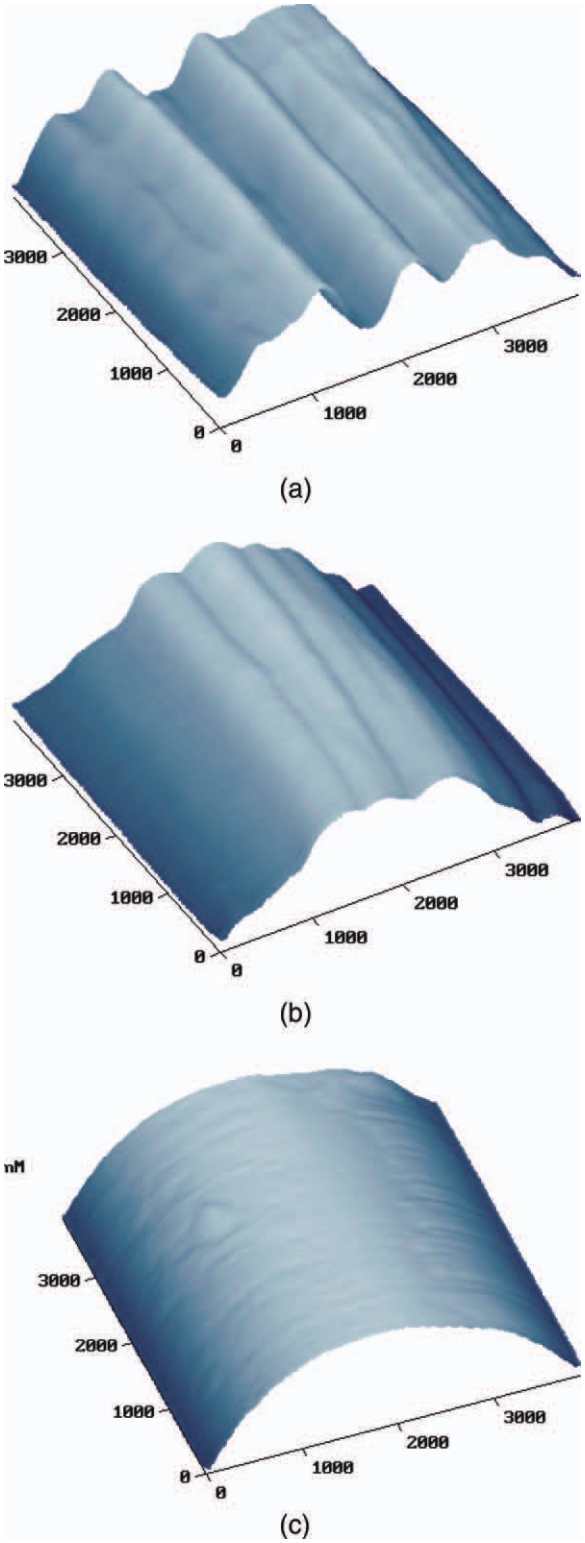


Figure 1 AFM images of different concentrations of sizing agent sized carbon fibers (a) C_1, (b) C_2, and (c) C_3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 2(e,f). However, the agglomeration of the sizing agent formed new defects and holes on the surface on the carbon fiber with the C_3 sizing agent.

Sizing content

The influence of different concentrations of the sizing agent on the sizing content of the carbon fiber was researched by the extraction, as shown in Figure 3. From Figure 3, the concentration of the sizing agent greatly influenced the sizing content of carbon fiber. The sizing content of C_1 sizing agent on the sized carbon fibers was 0.71%, while in the C_3 sized carbon fibers was 1.67 %. These results were consistent with the previous AFM, SEM research results.

The single tensile strength and Weibull distribution

Weibull distribution is being widely used in failure behavior analysis, especially for brittle materials, which is based on the series model of weakest link theorem. The Weibull distribution function is normally used to describe strength data.[11] The basic eqs. (2)–(7) for the model are below.

$$F(\sigma_f) = 1 - \exp[-L(\sigma_f/\sigma_0)^{\beta}] \quad (2)$$

L is a reference length and β is the Weibull shape parameter for lifetime. Both the σ_0 and β are the material constants. The higher β value could guarantee fewer defects in the carbon fiber. All parameters are determined based on the data obtained from stress rupture testing.

$$P = 1 - F(\sigma_f) = \exp[-L(\sigma_f/\sigma_0)^{\beta}] \quad (3)$$

For Weibull distribution, we take natural logarithm on both sides of eq. (3).

$$\ln\ \ln[1/(1 - F(\sigma_f))] = \beta \ln \sigma_f + \ln L - \ln \sigma_0^{\beta} \quad (4)$$

where the $F(\sigma_f)$ can be get by the below equation.

$$F(\sigma_f) = n/(N + 1) \quad (5)$$

N is the total fibers, and the n is the fracture number of the fibers under the tensile stress.

The tested strengths of fibers are arranged sequentially in an ascending order as $\sigma_1 < \sigma_2 < \ldots \sigma_i \leq \ldots \leq \sigma_n$, σ_i is the any of these tested strengths. The linear equation $Y = A + BX$ can be obtained from the curve fitting of $\ln\ln[1/(1-F(\sigma_f))]$ and $\ln\sigma_f$. According to B and A of the linear equation, σ_0 and $\beta = B$ are obtained by the eq. (6).

$$\sigma_0 = \exp\left(\frac{\ln L - A}{\beta}\right) \quad (6)$$

The statistical average intensity $\overline{\sigma}_f$ can be obtained by the following eq. (7).

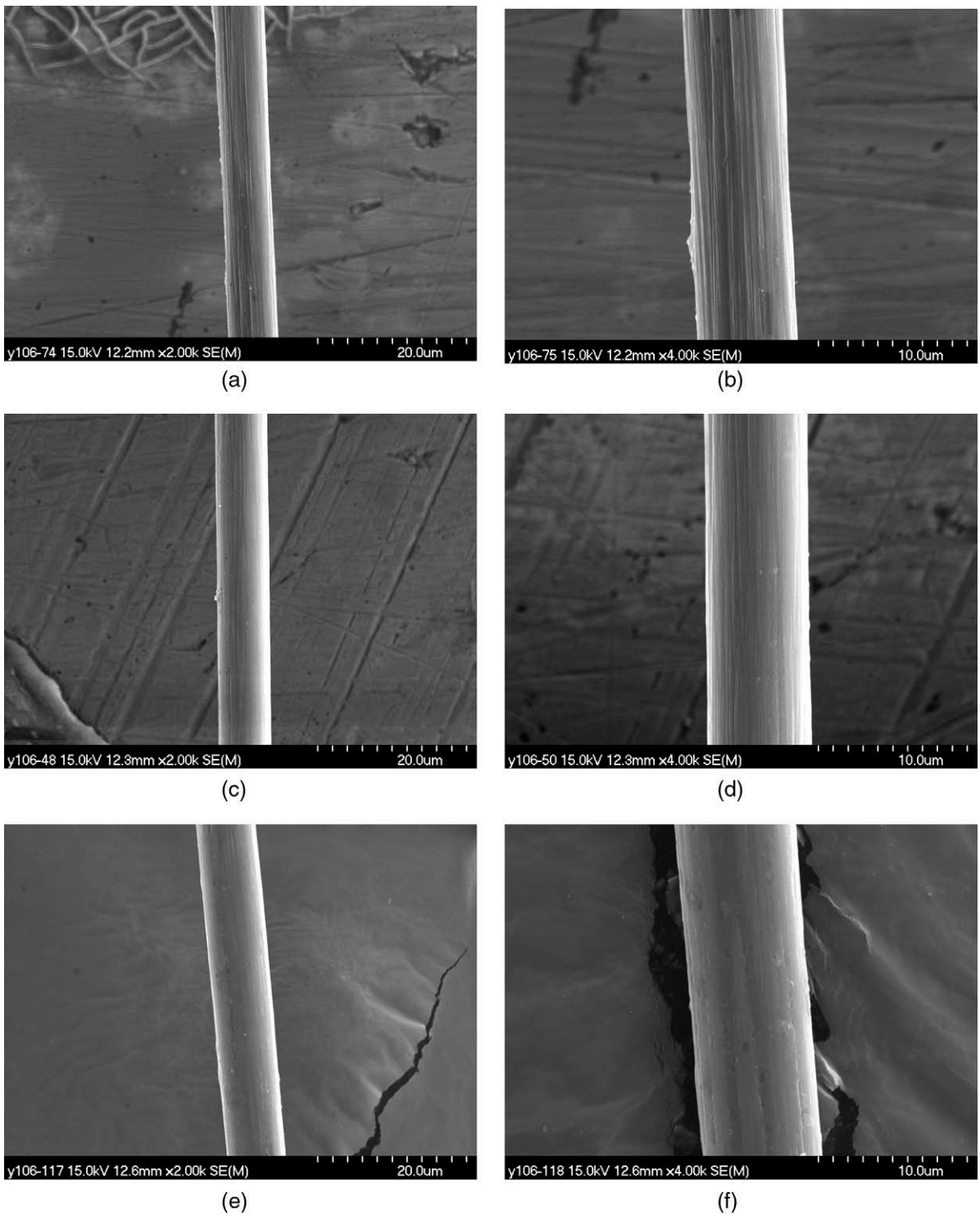


Figure 2 SEM images of different concentrations of sizing agent sized carbon fibers (a) and (b) C_1, (c) and (d) C_2, (e) and (f) C_3.

$$\bar{\sigma}_f = \sigma_0 L^{-1/\beta} \Gamma(1 + 1/\beta) \tag{7}$$

$\Gamma(\ )$ is the Gamma function.

From Figure 4, the Weibull parameters σ_f and R were typically derived. The Weibull distribution is a continuous probability distribution. It is an appropriate method to deal with carbon fiber strength. Linear plots indicate that the tensile force of single carbon fiber obey the single Weibull distribution.

From the fitted curve above, the tensile strength of sized fiber can be obtained, as shown in Table I. The tensile strength of the single carbon fiber was obviously different due to different concentrations of

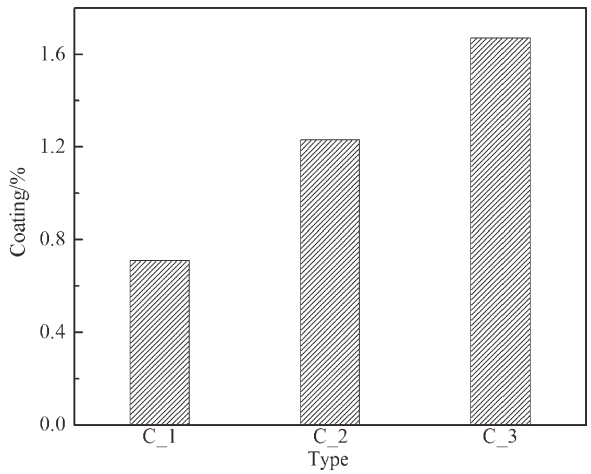


Figure 3 Coating thickness of the carbon fiber with different concentrations of sizing agent.

the sizing agent used for treatment. The tensile strength of carbon fiber sized with C_1 is 3.17 GPa, while the C_2 sized fiber is as high as 3.46 GPa, and the C_3 sized fiber is 3.34 GPa. The sizing agent on the fibers surface is beneficial to bridge the surface defects, reduce the external applied load, and improve the sensitivity of the tensile strength of carbon fiber. The uniform distribution of the C_2 sizing agent on the fibers surface assists in holding back excessive stress spreading in the flaws and changing the crack propagation paths. B ($\beta = B$) value shows carbon fiber surface defects. From Table I, the C_2 sized fiber has the maximum β value, which also shows carbon fiber surface has the fewest defects at this time. The results of β value agree with the SEM results well.

The sizing agent is particularly important for facilitating fiber handling during composite manufacture acting as a lubricant to prevent fiber damage.[4,5,8,9,12] But in actual applications, the excessive thickness of coating on the fibers is harmful to the handle ability of the carbon fibers yarn in processing and also waste resources. In order to obtain carbon fibers with adequate convergence and superior processability, the appropriate concentrations of the sizing agent is required.

Wettability

It has been also reported that the presence of sizing agent may improve the wetting performance of the fiber by the matrix resin and protect its reactivity.[5,13] The effect of different concentration of the sizing agent on the wettability of the carbon fiber in the epoxy-618 has been studied, and the results are shown in Figure 5.

Figure 5 shows that at the beginning, the absorption of the carbon fibers in the resin rapidly increased, shortly an inflection point appeared, and a balance has been reached after 4000 s. The concentration of sizing agent on the carbon fiber has certain influence the wettability. The wettability inflection

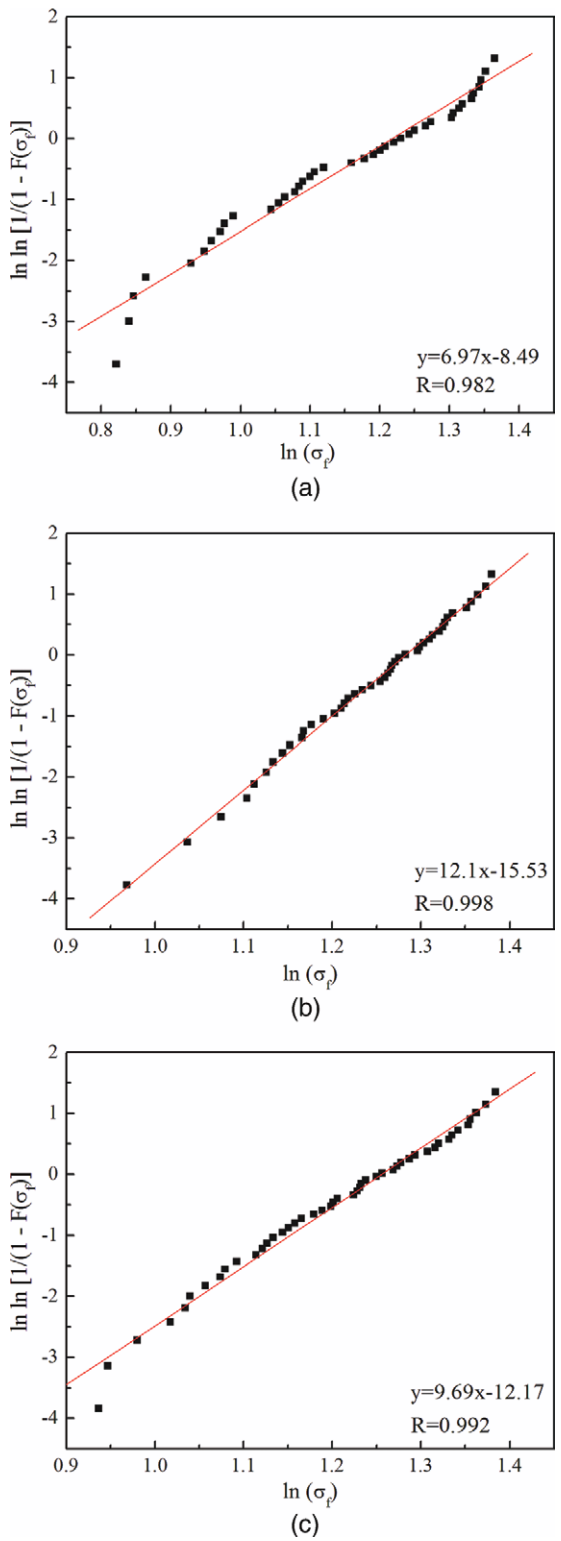


Figure 4 The Weibull distribution of different concentrations of sizing agent sized carbon fiber (a) C_1 and (b) C_2 and (c) C_3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
Tensile Strengths of Different Concentrations of the Sizing Agent Sized Carbon Fibers

Type	A	B	σ_0/GPa	*R*	*a*	σ_f/GPa
C_1	−8.49	6.97	1.92	0.982	0.94	3.17
C_2	−15.53	12.10	2.61	0.998	0.96	3.46
C_3	−12.17	9.69	2.34	0.992	0.95	3.34

point appeared at the same time in Figure 5. But the sizing agent C_1 sized carbon fibers had the least wettability speed, while the sizing agent C_2 sized carbon fibers had the biggest wettability speed.

Besides, the sizing agent plays an important role in the wettability of the carbon fibers. The sizing agent C_2 shows better wettability than others.

Interlaminar shear strengths (ILSS)

The effect of different concentration of the sizing agent on the mechanical properties of carbon fiber/epoxy (CF/EP) composites has been studied, and the results are shown in Figure 6. The interlaminar shear strength of the C_2 sized carbon fibers composites was higher than that of the C_1 and C_3 sized carbon fibers composites. The C_3 sized carbon fibers composite has the minimum interlaminar shear strength. As the small concentration of sizing agent sized carbon fiber, the sizing content was smaller, the fiber surface roughness to be retained, a large number of grooves can help increase the mechanical integration of fiber and resin accordingly. The coating on the fiber surface is advantageous to the interfacial adhesion and the chemical reaction with the resin. The high density of oxygen functional groups on the surface of the carbon fibers can also improve the adhesion properties. The high concentration of the sizing agent makes it easily distributed on the fiber surface and covers its grooves. The shallow grooves will reduce the mechanical integration. These also conform the results of the AFM and wettability.

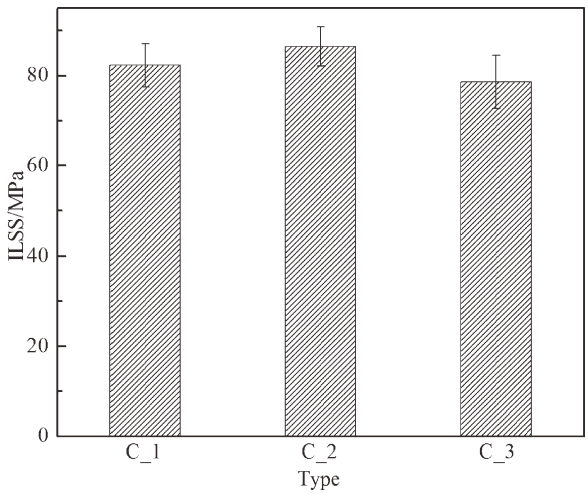


Figure 6 Effect of different concentrations of sizing agent on the ILSS.

The outstanding mechanical properties of the composites were not only dependent on the properties of the carbon fibers and the matrix, but also on the effectiveness of the interfacial adhesion between the carbon fibers and the matrix. Good interface bonding can increase the structural integrity of composites, which can help the load effectively transfer from the matrix resin to the fiber. The carbon fiber is extremely inert, usually untreated carbon fiber composite exhibits a weak bonding between fiber and matrix, giving the final composites with relatively low interlaminar shear strength.[14] The sizing layer, as the additional phase, significantly affects the final mechanical properties of the composites.[12,15]

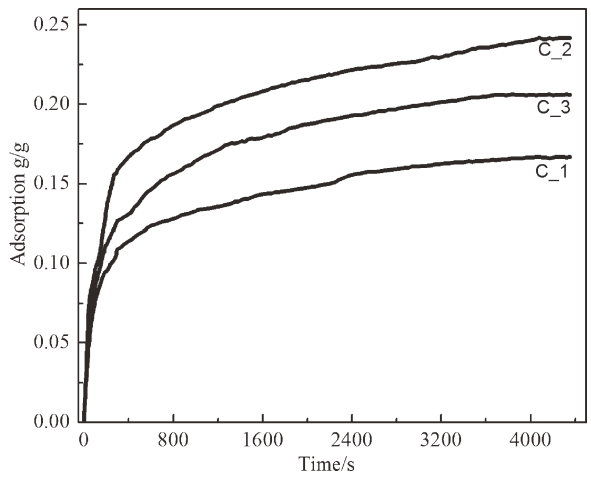


Figure 5 Effect of different concentrations of sizing agent on the wettability.

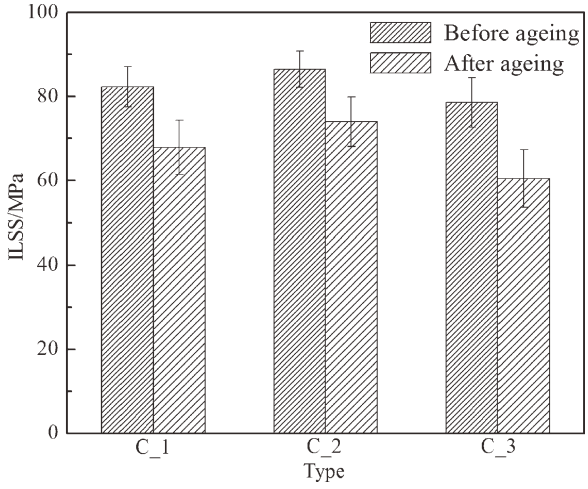
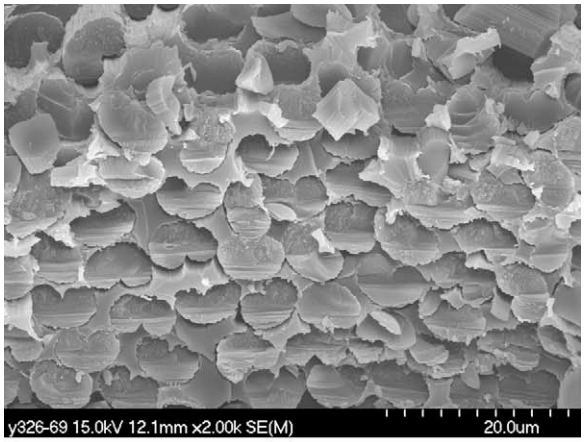
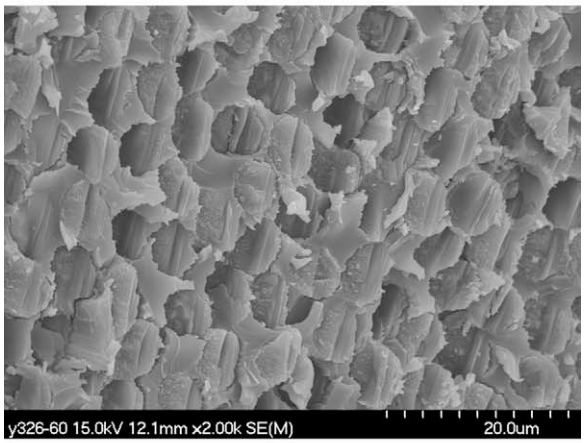


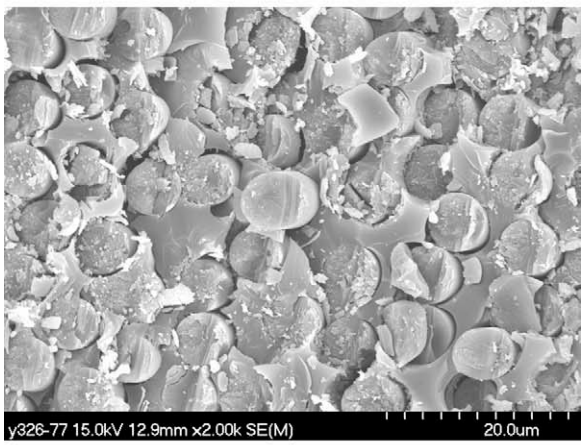
Figure 7 Effect of different concentrations of sizing agent on the hygrothermal aging performance.



(a)



(b)



(c)

Figure 8 SEM images of the fracture sections of different concentrations of sizing agent sized carbon fiber/Epoxy resin composites (a) C_1 and (b) C_2 and (c) C_3.

Ageing resistance

It can be seen in Figure 7 that the interlaminar shear strength decreased after the hygrothermal ageing treatment. After the hygrothermal ageing, the interlaminar shear strength of the CF/EP composites decreased to 17.57%, 14.49%, and 23.03% with the carbon fibers sized by C_1, C_2, C_3, respectively. It is considered that the paths of crack propagation under shear stress are decided by the stress field of the crack tip and the mechanical properties of the matrix and the fibers.[16] The good performance in the hot and humid environment is an important problem of the CF/CP composites.

Further characterization of the composites after the hygrothermal ageing test was performed by SEM. As shown in Figure 8, the possible schematic of crack propagation paths at the interphase between the fibers and the matrices appear to be varied. The sizing agent uniformly distributed on the fibers surface and assisted to fill up the weak microregions of the interphase, acting as a binding bridge. Furthermore, the chemical interactions at the matrix/sizing layer/fiber interfaces are improved.

The holes on the fracture section of the composites with sizing agent C_1 are observed in Figure 8(a). Figure 8(c) displays the carbon fibers pullout and holes on the fracture section of the composites with sizing agent C_3, which shows the weak interfacial adhesion. Compared to the sample with sizing agent C_1 and C_3, the carbon fiber composites sized with the C_2 exhibit evidently a better interfacial bonding [Fig. 8(b)]. It is clearly seen that the boundary between the fiber and the matrix is not clear, presenting the ideal compact integrity surface.

CONCLUSIONS

The results of this study revealed that the different concentrations of sizing agent significantly changed carbon fibers surface characteristics and its interface properties. The AFM and SEM results indicated that the sizing agent changed the surface topography of the fibers. Different concentrations of the sizing agent have different contributions to the wetting performance of carbon fibers. The single fiber strengths and Weibull distributions of the C_2 sized carbon fibers were better than that of carbon fibers sized with other concentrations. Finally, ILSS and ageing resistant properties indicated that the sizing agent C_2 on the carbon fibers surface was better than that of the C_1, C_3 sizing agent.

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