

Preparation and Properties of Water-Soluble-Type Sizing Agents for Carbon Fibers

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ABSTRACT: A water-soluble epoxy resin was synthesized by the reaction between novolac epoxy resin (F-51) and diethanolamine. Then, the modified F-51 was mixed with poly(alkylene glycol allyl glycidyl ether) as a film former of a sizing agent. A series of water-soluble sizing agents for carbon fiber (CF) were prepared. The modified F-51 was analyzed by Fourier Transform infrared spectroscopy. The surface morphology of the CF was characterized by scanning electron microscopy. The effects of the sizing agent on the handling characteristics were investigated by abrasion resistance, fluffs, and breakage and stiffness tests. The results show that the abrasion resistance of the sized CF increased by 114.5% and reached 2344 times and the mass of fabric hairiness decreased to 3.2 mg. The interlaminar shear strength (ILSS) test indicated that the interfacial adhesion of the composite could be greatly improved. The ILSS of the sized CF composite could reach a maximum value of 42.40 MPa. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39843.

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INTRODUCTION

Carbon fiber (CF) is widely used as a reinforcing material in composites, especially in advanced composites, because of its outstanding properties, including its high specific strength, corrosion resistance, and low density.^{1,2}

CF needs to be woven before it is used. Because of the brittleness of CF, many problems, such as filament breakage and fluffing, arise during the fabrication process.³ Excessive fluffing may hinder the weaving process and lower the quality of the CF. In addition, because the pristine surface of CF is a nonpolar compound of highly crystallized graphitic basal planes with inert structures, the interfacial adhesion between the CF and resin matrix is poor.^{4,5} As a result, the ideal mechanical properties of composites cannot necessarily be achieved. Therefore, CF is generally sized or coated by a sizing layer on the surface.^{6–9} The sizing layer could protect CF, and one can obtain a clustering effect to spin the fiber and reduce hairiness. The presence of a sizing agent may also ameliorate the wettability of the fiber, and this contributes to the adhesion between the fiber and matrix. Furthermore, the sizing layer plays a key role in transferring stress from the matrix to the fiber.

The previous work has mainly focused on emulsion-type sizing agents, which are generally prepared by a phase-inversion emul-

sification method. However, the inevitable problems in the process of sizing agent storage and usage are as follows:

1. Demulsification may happen when an emulsion is stored for a long time.
2. The effective constituent may precipitate out when the emulsion system is diluted below 5% solid content.
3. The synthetic route of some components is complicated.

A water-soluble sizing agent has advantages in some aspects compared with the emulsion-type one. A water-soluble sizing agent possesses great stability in storage and agitation. In addition, it is easily prepared because of its excellent water solubility. Meanwhile, there is no environmental pollution during the process of preparation and usage.

In our study, polyfunctional group novolac epoxy resin (F-51) and diethanolamine (DEA) were used to synthesize a modified epoxy resin. Sizing agents, composed of the water-soluble modified epoxy resin, poly(alkylene glycol allyl glycidyl ether) (AEPH), and other assistants, were prepared. The influence of the self-made sizing agents on CF was investigated by multiple testing methods. The handling characteristics of CF were evaluated by the fabric hairiness, stiffness, and abrasion resistance tests. The interfacial adhesion properties were evaluated by an interlaminar shear strength (ILSS) test. Scanning electron

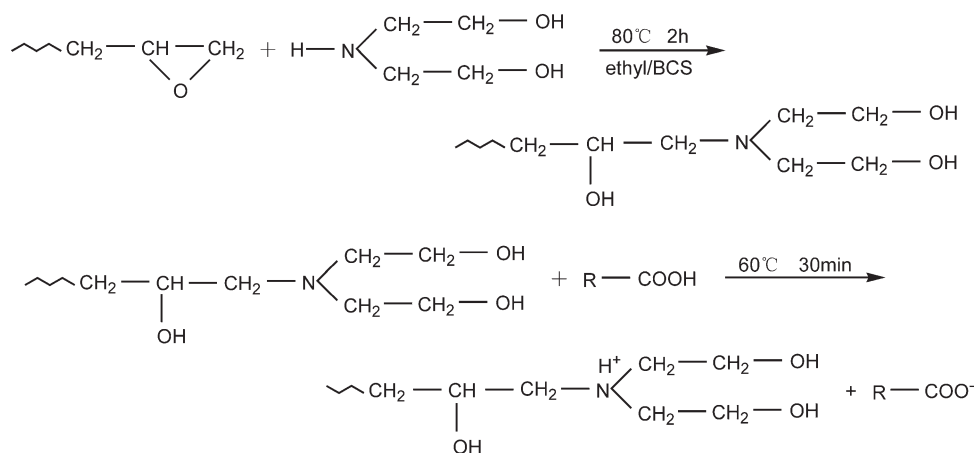


Figure 1. Reaction route for the modified epoxy resin.

microscopy (SEM) was used to analyze the surface morphology of the CF and the interface of the composites.

EXPERIMENTAL

Materials

F-51 was supplied by Yisheng Resin factory China [viscosity = 6.8 Pa s, epoxy value (EV) of 0.50–0.55]. Epoxy resin (E-51) was supplied by Yisheng Resin Factory China (EV = 0.50–0.55). Absolute alcohol, DEA, ethylene glycol monobutyl ether, and acetic acid were purchased from Tianjin Guangcheng Chemical Reagent Corp. (China). Triethylenetetramine (TETA) was purchased from Aladdin Chemical Reagent Corp. (China). The penetrant, 2-octanol poly(oxyethylene ether) (JFC-2), was purchased from Jinan Chuanglong Chemical Co. T700 (12,000) CF was obtained from Toray Co. (Japan). AEPH was supplied by Hangzhou Diweilai Co.

Preparation of the Modified Epoxy Resin

The epoxy group ring was polar and easy to open under the attack of nucleophiles. In our study, the nucleophile DEA reacted with the F-51 resin to prepare a water-soluble resin. Hydroxyls were formed on epoxy resin chains. After neutralization by acetic acid, the modified resin could dissolve in water.¹⁰ The reaction route is shown in Figure 1.

F-51 resin was added to a three-necked flask and heated for 10 min at 60°C under a constant stirring rate. A certain percentage of mixed solvent consisting of absolute ethyl alcohol and ethylene glycol monobutyl ether was added to the flask to dissolve the resin. The system was heated to 80°C. The DEA solution (dissolved in ethyl alcohol) was dripped into the flask.¹¹ Then, we kept stirring the solution for 2 h at 80°C. Thereafter, we decreased the temperature to 60°C. A quantity of acetic acid solution, whose gram equivalent was equal to that of the DEA, was dripped into the modified resin and stirred for 30 min at 60°C. Finally, the solvent was wiped off by a rotary evaporator, and the waterborne F-51 system was obtained.¹⁰

Preparation of the Sizing Agent and Sizing Treatment of CF

F-51 resin reacted with DEA at mass ratios of 85:15, 75:25, and 65:35 (ideal epoxide group opening ratios = 1:3, 2:3, and 1, respectively). Then, the modified F-51 resin was mixed with

AEPH at mass ratios of 70:30, 80:20, and 90:10 thoroughly to produce film formers. The chemical structures of the modified F-51 resin and AEPH are shown in Figure 2. A quantity of 2% total mass of the penetrant JFC-2 was added. The sizing agent was gained after the mixture was diluted to a 1% solid content with deionized water. The compositions of the series of sizing agents are recorded in Table I.

To remove the sizing agent coated on the commercial CF surface, T700 CF was refluxed in acetone for 36 h with a Soxhlet apparatus, washed repeatedly with deionized water, and dried *in vacuo* at 100°C for 12 h.¹² A dipping method was used in the sizing process. The CF was immersed in the sizing agent for 30 s by use of a dip tank in conjunction with automatic processing equipment for continuous running of CF. Then, the CF was dried at 100°C for 20 min.^{13,14}

Characterization

Chemical Structure of the Modified Resin. The chemical structures and compositions of the F-51 resin and modified resin were analyzed with a Nicolet 380 infrared spectrometer (Thermo Electron Corp.). The specimens were prepared by the method of smearing resin onto a KBr salt window.

Conversion Rate of the Epoxy Groups. The EVs of the unmodified F-51 and modified epoxy resin were measured by the hydrochloric acid–acetone method according to GB 1677-

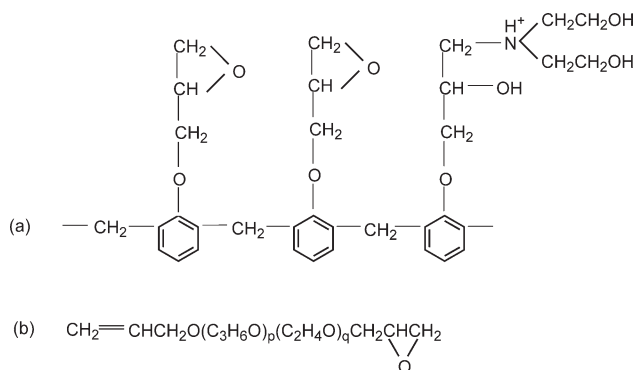


Figure 2. Chemical structures of the (a) modified resin and (b) AEPH.

Table I. Compositions of the Sizing Agents

Composition/Specimen	A1	A2	A3	B1	B2	B3	C1	C2	C3
F-51/DEA reaction mass ratio	85:15	85:15	85:15	75:25	75:25	75:25	65:35	65:35	65:35
Modified resin/AEPH mixture mass ratio	70:30	80:20	90:10	70:30	80:20	90:10	70:30	80:20	90:10

81. Then, the conversion rate of the epoxy groups (α ; %) was calculated by eq. (1):

$$\alpha\% = (X_0 - X_i) / X_0 \times 100\% \quad (1)$$

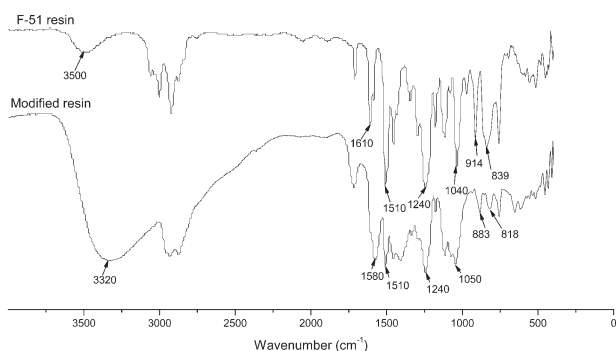
where X_0 is the epoxy value of the unmodified F-51 and X_i is the epoxy value of modified F-51.¹¹

Surface Morphology of the CF. The surface morphology of the sized and desized CFs was observed with a Hitachi 2500 SEM (Hitachi Co., Japan) with an accelerating voltage of 10 kV.¹⁵ The specimens were treated by a spray-gold process.

Test of the Fabric Hairiness. The hairiness was measured according to a Japanese patent.¹⁶ A fiber bundle was passed through two polyurethane sponges (40 × 10 × 5 mm) at rate of 1 m/min; the load of the sponge was 200 g. After 10 min, the amount of hair attached to the sponges was calculated. Five CF bundles were measured, and the average hairiness was recorded.¹³

Test of the Abrasion Resistance. The abrasion resistance was tested by an LFY-109B fiber abrasion tester (Shandong Textile Academy). The diameters of the guide rollers and stainless rod were 10 and 15 mm, respectively. The frictional angle of the stainless rod and two guide rollers was 120°, with a load of 100 g. The CF bundle was reciprocatingly abraded by a stainless steel roll at a rate of 120 times/min until all of the fiber fractured. Five CF bundles were measured, and the average abrasion resistance numbers were recorded.

Stiffness of the CF. An unwound CF bundle was obtained according to ISO 3375-2009. The stainless steel hook (radius = 10 mm) was made of a stick (radius = 5 mm). There was a sliding scale at a standard distance of 60 mm below the suspension point. First, the CF bundle (500 mm) was suspended. Its center was hung on the stainless steel hook. The distance of the two hanging ends of the CF was measured by a sliding scale after 30 s. Five CF bundles were measured, and the average stiffness value was recorded.¹³

**Figure 3.** Fourier transform infrared spectra of the F-51 resin and the modified resin.

ILSS of the CF/Epoxy Resin Composite. The ILSS of the CF-reinforced composite was tested by a three-point, short-beam shear method according to ASTM D 2344.¹⁷ The specimens were prepared by resin-transfer molding. The poured resin was epoxy resin E-51, and the curing agent was TETA. The mass ratio of E-51 to TETA was 100:12. The crosshead speed was 1 mm/min. The values of ILSS were calculated by eq. (2):¹⁸

$$ILSS = 3P_b / 4bh \quad (2)$$

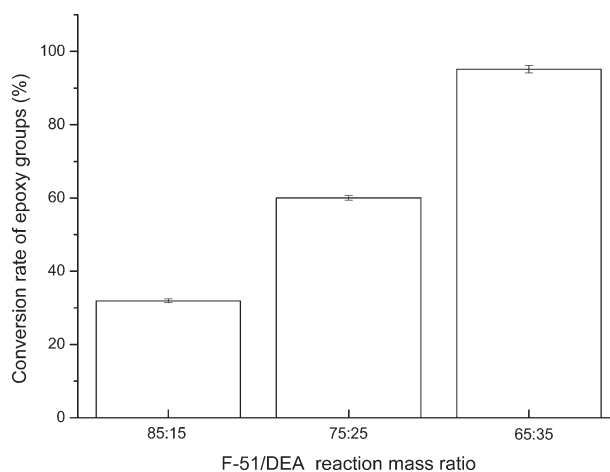
where P_b is the failure load and b and h are the specimen width and thickness, respectively.

RESULTS AND DISCUSSION

Chemical Structure of the Modified Resin and Conversion Rate of the Epoxy Groups

Figure 3 shows the Fourier transform infrared spectra of the F-51 resin and the modified resin (F-51/DEA reaction mass ratio = 85:15). In the spectra of the F-51 resin, 914 and 839 cm^{-1} were the characteristic absorption peaks of the epoxy groups. The peak at 1040 cm^{-1} was the absorption peak of the primary alcohol (C-O) stretching vibration. The peak at 1240 cm^{-1} was the absorption peak of aryloxy. The peaks at 1610 and 1510 cm^{-1} were the characteristic absorption peaks of the benzene ring. Finally, the peak at 3500 cm^{-1} was the absorption peak of the hydroxyl group.

Because of the addition reaction between the F-51 resin and DEA, part of the epoxide groups took part in a ring-opening reaction. This led to the decrease of the absorption peak of the epoxide groups at 883 and 818 cm^{-1} in the spectra of the modified resin. Meanwhile, the absorption peak at 3320 cm^{-1} grew deeper and wider because of the introduction of hydroxyl groups and its hydrogen bonds produced by the ring-opening

**Figure 4.** Conversion rate of the epoxide groups.

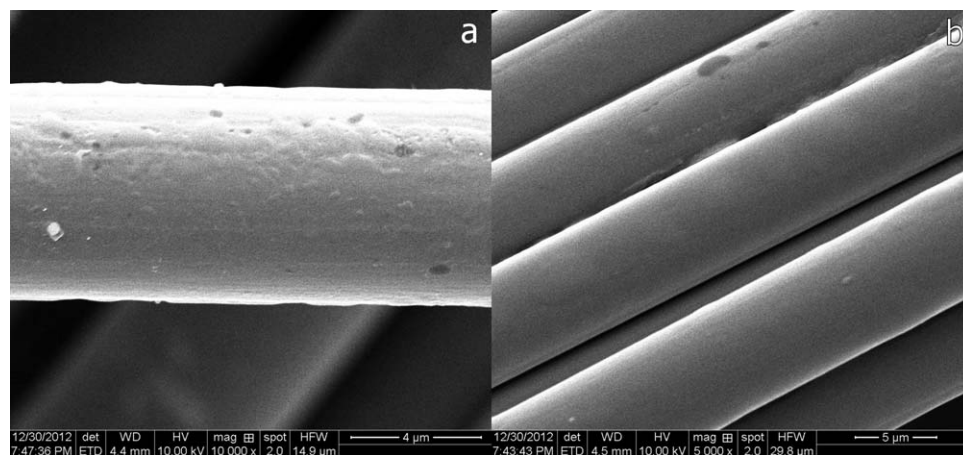


Figure 5. SEM images of different CFs: (a) desized CF and (b) sized CF (sized with the sizing agent A1).

reaction and DEA. These results prove that the reaction occurred according to the molecular design.

The epoxide group conversion rates with different F-51/DEA reaction mass ratios were investigated and are recorded in Figure 4.

As we observed, the conversion rate of the epoxide groups increased as the mass ratio of F-51/DEA increased. The conversion rates of the epoxide groups were 31.93, 60.01, and 95.15% when the F-51/DEA reaction mass ratios were 85:15, 75:25, and 65:35, respectively.

Surface Morphology of the CF

The change in the CF surface morphology was detected by SEM, and the results are shown in Figure 5.

The images reveal the difference between the desized and sized CFs (sized with the sizing agent A1). Figure 5(a) shows lots of irregular embossments and hollows on the surface of the desized CF. Meanwhile, as shown in Figure 5(b), the sized fiber surface was smooth with few defects. Obviously, the CF surface was covered with a layer of the continuous sizing agent film. This could protect the CF from wearing out and repair the deficiencies on the fiber surface. The film could improve the durability and handling characteristics of the CF.¹⁹

Handling Characteristics

The results of the abrasion resistance and hairiness tests are shown in Table II.

The results clearly demonstrate that the sizing agents not only improved the abrasion resistance of CF but also greatly reduced the amount of fabric hairiness. The maximum abrasion resistance reached 2344 times, increasing by 114.5% compared with

the desized one (1093 times). It was also higher than that of the commercial T700 CF (1838 times). The minimum fabric hairiness was just 3.2 mg, approaching that of the T700 CF (3.1 mg), whereas the desized one was 11.7 mg.

During the weaving process, the mechanical friction acted repeatedly on CFs. At first, the surface cracked when the fiber bundle was worn. Then, fabric hairiness emerged under a bending force and shear force. Fabric hairiness made the tensile strength and shear strength of the CF decrease and the friction coefficient increase. Furthermore, part of carbon filaments broke down to form wool balls. The friction area between the wool balls and fiber bundles expanded, and more filaments got damaged. Finally, the fiber bundle was broken at one weak point.²⁰ On the one hand, the tough sizing agent film on the fiber surface prevented the fiber filaments from abrasion. On the other hand, the sizing agent was subject to a clustering effect for CF and compacted the yarns.

As judged from Tables I and II, the higher the mass ratio of AEPH was in the sizing agent, the higher abrasion resistance of the sized fiber was. The epoxy resin sizing film was rigid and brittle. A friction force easily led to the breakage and falling off of the brittle sizing film from the fiber surface, which decreased the abrasion resistance of the CF.²¹ Traditionally, polymers have high flexibility when they consist of single bonds, as single bonds have the ability to internally rotate.²² AEPH possesses excellent flexibility as a result of its long, single-bond chain and the numbers of ether bonds. It can form stress relaxation at the crack tip, restrain crack propagation, and make plastic deformation occur when a load acts on the film. Accordingly, the presence of AEPH boosts the capacity of toughness, crack resistance, and elasticity of a sizing film to some extent.^{23,24}

Table II. Abrasion Resistance and Hairiness of the Sized and Desized CFs

Specimen	A1	A2	A3	B1	B2	B3	C1	C2	C3	T700 CF	Desized CF
Abrasion resistance/time	2051 ± 109	2029 ± 97	1938 ± 92	2344 ± 104	2231 ± 99	2031 ± 110	2117 ± 96	2043 ± 90	2103 ± 97	1838 ± 86	1093 ± 49
Hairiness/mg	3.2 ± 0.1	4.5 ± 0.2	5.2 ± 0.2	4.7 ± 0.1	5.1 ± 0.1	3.6 ± 1.0	4.2 ± 0.2	5.1 ± 0.1	3.8 ± 0.2	3.1 ± 0.1	11.7 ± 0.3

Table III. Stiffness Data for Sized and Desized CF

Specimen	A1	A2	A3	B1	B2	B3	C1	C2	C3	T700 CF	Desized CF
Stiffness (mm)	73 ± 2	76 ± 2	78 ± 3	65 ± 4	73 ± 3	79 ± 2	65 ± 3	70 ± 4	79 ± 2	76 ± 3	23 ± 3

Stiffness can reflect the flexibility of CF. As shown in Table III, the stiffness of the sized fibers ranged from 70 to 79 mm and approached that of T700 CF (76 mm). The stiffness of the desized fibers was just 23 mm.

Repetitive bending stress acted on the CF during the weaving process. The CFs could be curved to a wide winding angle when they were woven, especially into a fractal texture. The weaving process went on smoothly only when the stiffness was appropriate.

A traditional pure epoxy resin sizing agent film might make a CF stiff and inflexible, and this leads to poor handling characteristics of the fibers and low impact resistance of composites.²⁵ In this study, AEPH was used to ameliorate the rigidity and stiffness of the epoxy resin sizing agent film. Moreover, sized CFs with diverse handling characteristics were obtained when the resin/AEPH mass ratio changed; these would fit different processes in engineering. For example, in the production of chopped fibers, the CF must remain stiff to endure the cutting force. Accordingly, a sizing agent could be used in chopped fibers when the mass ratio of the AEPH decreases.

ILSS of the CF Composites

The ILSS values of the composites based on the CFs with different sizing agents are shown in Figure 6.

As shown in Figure 6, the ILSS improved after the fiber was sized. The composite with CF sized with sizing agent A3 obtained the maximum value of 42.40 MPa; this approximated the value of the T700 CF (42.97 MPa), increasing by 24.5% compared with the desized one (34.05 MPa). The results indicate that the sizing agent layer could bond the fiber with the matrix and pass the stress from the matrix to the fiber.

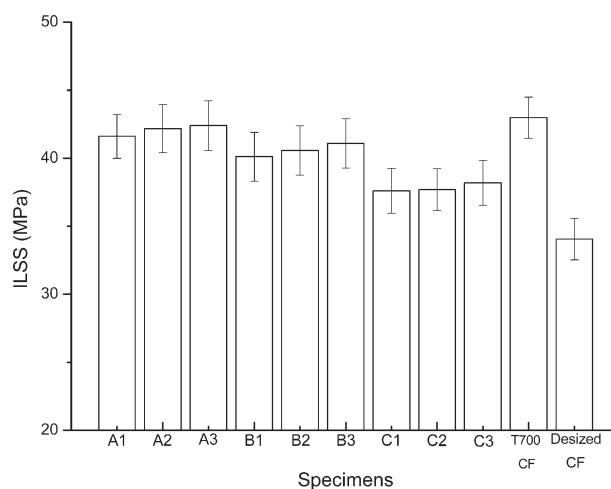
Between the CF and the matrix, there were chemical binding forces, Van der Waals forces, and mechanical anchor forces. The leading role was the chemical binding force, and the others were auxiliary.²⁶ A requirement for excellent bonding is the good wettability of the fiber. Because the chemical structure of the film former is similar that of the matrix, the epoxy resin could wet the fiber completely.^{27,28} In addition, both the modified epoxy resin and AEPH had enough epoxide groups to crosslink with the matrix resin during the matrix curing. All of these factors contributed to the interfacial adhesion.²⁹

As shown in Figure 6, the ILSS decreased with increasing epoxide group opening rate. According to the similarity–intermiscibility theory, the excellent wettability of the fiber could be obtained when the matrix resin and film former have the same active groups and group polarity.^{30,31} The introduction of polar oxygen groups onto the fiber surface led to an increase in the surface energy; this was reported to improve the wettability of fibers to some extent.³² However, increasing the CF surface

energy alone is not sufficient to improve the wetting behavior and, therefore, the interfacial adhesion between the fiber and the matrix resin. Having a combination of an appropriate fiber surface treatment and a matrix formulation that allows direct chemical reaction is far more effective for sufficient interfacial adhesion of a CF composite.³³ Although the epoxide ring-opening reaction produced some hydroxyl radicals, which led to an increase in the fiber surface energy, the polarity and molecular structure of the modified resin became more different than the matrix resin. Also, with the increase in the epoxide group opening rate, the reaction rate of the TETA, E-51 resin, and modified F-51 decreased; this resulted in a lower interfacial adhesion force between the sized CF fiber and the matrix resin. Synthetically, when more epoxide groups were opened, this led to decreases in the wettability of the CF and the interfacial adhesion.

To intuitively investigate the interfacial adhesion, the fracture surfaces of the composites were treated by a spray-gold process and were examined by SEM. Figure 7(a) shows that the desized CF was entirely separated from the matrix, and gaps existed in the fiber/resin interface. Little resin remained on the surface of the drawn CF, and numerous holes were left in the matrix. The adhesion between the CF and matrix was poor because of the poor compatibility between the CF and matrix resin.

Figure 7(b) shows the fracture surface of the composites with CF sized with the sizing agent A1. As shown in Figure 7(b), there was more matrix resin around the interface than that of the desized one. This indicated that the adhesive force in the CF/resin interface was improved after the sizing treatment. When interfacial failure occurred on the composite, stress could be transferred from matrix to fibers through the sizing film.³⁴ This increased the ILSS values of the CF composites.

**Figure 6.** ILSS of the CF composites with different sizing agents.

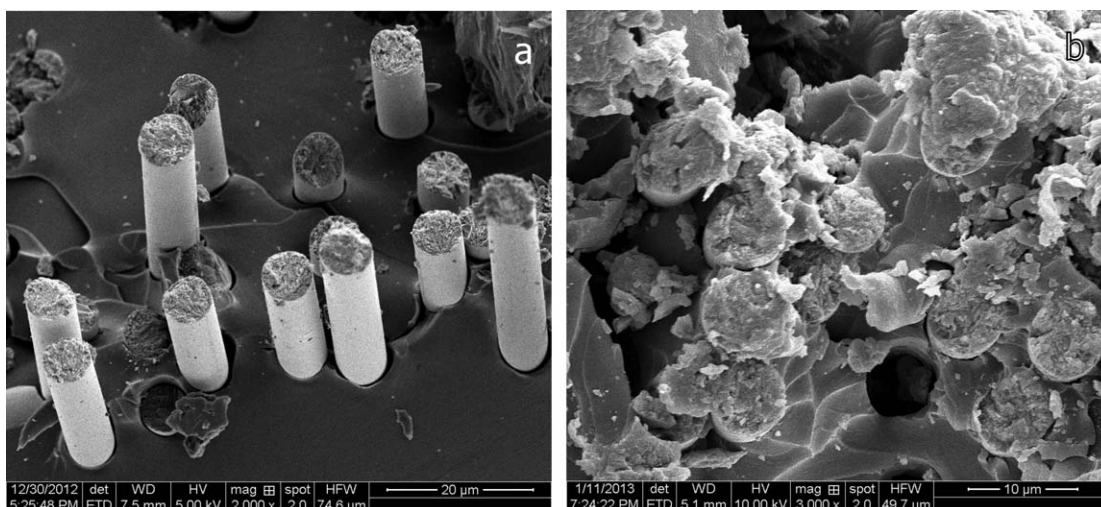


Figure 7. SEM images of the fracture surfaces of the composites with (a) desized CF and (b) sized CF (sized with the sizing agent A1).

CONCLUSIONS

The water-soluble type sizing agent dissolved in water steadily and was easy to prepare. AEPH was applied to modify the brittleness and rigidity of the pure epoxy resin sizing agent film. Synthetically, the best properties of the sizing agent could be obtained when the F-51 resin was reacted with DEA at mass ratio of 85:15 and modified epoxy resin was mixed with AEPH at a mass ratio of 70:30. The abrasion resistance of the sized CF could reach 2051 times. The amount of fabric hairiness was just 3.2 mg. The stiffness (73 mm) was appropriate. The ILSS of the sized CF composite could reach 41.61 MPa and obtain a 22.2% improvement compared with that of the desized one.

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