Preparation of emulsion-type thermotolerant sizing agent for carbon fiber and the interfacial properties of carbon fiber/epoxy resin composite

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ABSTRACT: A modified resin was synthesized through the reaction between dodecylamine and tetraglycidyldiaminodiphenylmethane (TGDDM), which was used as the film former of sizing agent for carbon fiber (CF). The sizing agents were prepared through phase inversion emulsification method. Fourier transform infrared spectroscopy (FTIR) was utilized to analyze the modified resin. Particle sizes of the sizing agents were tested to evaluate their stabilities. Differential scanning calorimetry (DSC) results demonstrated that the glass transition temperature (T_g) of the modified TGDDM is much higher than the T_g of the cured epoxy resin E-44. The influences of the sizing treatment on CF were investigated by abrasion resistance, fluffs, and stiffness tests. The maximum abrasion resistance increased by 172.8%, compared with the abrasion resistance of the desized CF. Interlaminar shear strength (ILSS) results of the CF/TGDDM composites indicated that the interfacial adhesion between CF and matrix resin was greatly improved after CF was sized. The maximum ILSS value could obtain a 29.16% improvement, compared with the ILSS of the desized CF composite. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2015, 132, 41882.

INTRODUCTION

Carbon fiber (CF) is widely used as reinforcing material in composites, especially in advanced composites due to its outstanding properties with respect to particular light weight, remarkable corrosion resistance, high specific strength and modulus.[1–5] However, as CF is brittle in nature, many problems, such as fluffs and filament breakages, arise during weaving manufacturing process.[6,7] Therefore, surface modification of CF is essential. Sizing treatment of CF is an efficient method for improving the handleability of CF yarn and effectively hindering the occurrence of hairiness and breakage of CF bundle in subsequent process.[8,9] In addition, sizing agent can also greatly ameliorate surface wettability of CF and make CF surface more active.[10–12]

The previous researches[13–16] regarding the film formers of emulsion-type epoxy-sizing agents have been mainly concentrated on traditional epoxy resins. Most of the generally employed epoxy resins belong to diglycidyl ether of bisphenol A (DGEBA), such as E-54, E-51, and E-44. DGEBA-type epoxy resins have a main drawback, that is, dissatisfactory heat resistance. Consequently, DGEBA-type sizing agent cannot meet the

need of cutting-edge fiber-reinforced structural composites in some particular fields. Some efforts have also been devoted to the research of thermoplastic-type sizing agent.[17,18] By using some heat-resistant thermoplastic resins, such as polyetherimide (PEI) and poly(phthalazinone ether ketone) (PPEK), as the film formers of sizing agents, the emulsion-type sizing agents can be obtained. However, most thermoplastic resins have lower solubilities that lead to a poor workability.

Multifunctional epoxy resins possess better heat resistance in practical applications, mainly because they are higher cross-linking network after cured.[19] Unfortunately, the higher cross-linking density leads to brittleness of the resin.[20] Accordingly, the toughness of the multifunctional epoxy resins should be improved before used as the film formers of sizing agents. A relatively effective toughening method is blending thermoplastics with the resins.[21] Multifunctional epoxy resins that were toughened by some high-performance thermoplastic resins have been adequately investigated in Kim B. S. et al. studies.[22] But toughening epoxy resins by means of inserting aliphatic chains that are able to readily internally rotate into the resins was less reported in previous works.[23]
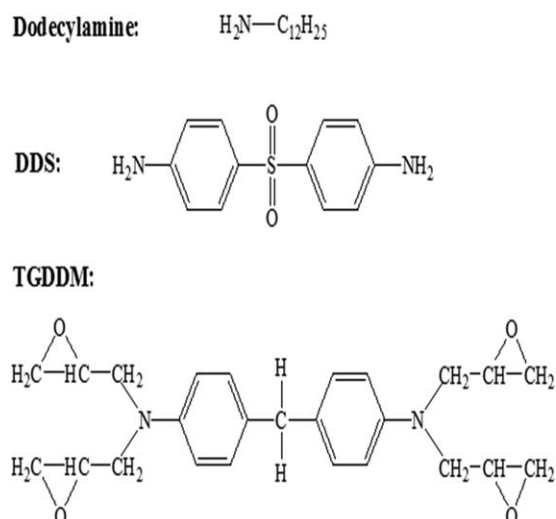
Figure 1. Chemical structures of dodecylamine, DDS, and TGDDM.

The objective of this study is to develop a new kind of epoxy-type sizing agent for CF which possesses both excellent heat resistance and good toughness. In this work, tetraglycidyldiaminodiphenylmethane (TGDDM) and dodecylamine were used to synthesize the modified epoxy resin, which was used as the film former of sizing agent. Inserting the flexible chains into TGDDM could effectively improve toughness but only slightly decrease the heat resistance of the film former. Then, sizing agent was prepared through phase inversion emulsification method. The thermostability of sizing agent was evaluated by DSC test. The influence of the sizing treatment on the CF was investigated by the stiffness, fabric hairiness, and abrasion resistance tests. Scanning electron microscope (SEM) was utilized to observe the microstructures of the sized CF, desized CF, and the fracture surface of CF/TGDDM composite. The interfacial adhesion of CF/TGDDM composite was examined by interlaminar shear strength (ILSS) test.

EXPERIMENTAL

Materials
TGDDM [viscosity of 10.7 Pa·S (25°C), epoxy value (EV) of 0.75–0.85] and diaminodiphenyl sulfone (DDS) were supplied by Hubei Zhenzhengfeng Material Factory, China. Epoxy resin E-44 (EV of 0.40–0.47) was supplied by Yisheng Resin Factory, China. Dodecylamine and nonylphenol polyoxyethylene ether (NP-10) were purchased from Jiangsu Haian Petrochemical Plant, China. Pesticide emulsifier 1601 was supplied by Hubei Xingtai Chemical Corp., China. Acetone and neopentyl glycol diglycidyl ether (diluent 678) were purchased from Aladdin Chemical Reagent Corp., China. CF (T700 SC, 12 K) was purchased from Toray Co., Japan. Chemical structures of dodecylamine, DDS, and TGDDM are shown in Figure 1.

Synthesis of Modified TGDDM
Because the electronegativity of "C" and "O" is different, the epoxy group is polar enough to open under the attack of nucleophiles.[24] The reaction between nucleophile dodecylamine and TGDDM was applied to synthesize the modified resin. The flex-ible aliphatic chains ($-C_{12}H_{25}$) were connected to TGDDM molecules.

TGDDM was added into a three-necked flask and heated for 20 min at 50°C under a constant stirring rate. Thereafter, a certain stoichiometry of dodecylamine was dissolved in acetone. The mixture was then added into the three-necked flask with a constant voltage dropper at a constant dropping rate of 5 mLmin^{-1}. Meanwhile, the heating temperature of the system was increased to 80°C.[25] The modified resin was obtained after 100 min. The compositions of the modified resins are listed in Table I.

Preparation of Emulsion-Type Sizing Agent
Phase-inversion emulsification method[26] was used to prepare the sizing agent. The emulsifiers were 1601 and NP-10 (1 : 1 by mass). The modified resin (MR1, MR2, MR3, MR4, and MR5 were the film formers of SA1, SA2, SA3, SA4, and SA5, respectively) and emulsifiers were mixed and added into a beaker at a mass ratio of 10 : 1. Thereafter, reactive diluent 678 (the mass ratio of 678 to resin was 1 : 10) was added to the above mixture, which could decrease the viscosity of the modified resin. Next, the mixture was dispersed by a digital display shear emulsifying machine under a constant stirring rate of 11000 rmin^{-1} at 50°C. Deionized (DI) water (the mass ratio of resin to deionized water was 1 : 4) was then dripped into the beaker at a constant dropping rate of 2 mL min^{-1}. With the increase in deionized water content, the phase of the system changed from water-in-oil to oil-in-water. The reasons to the phase inversion of the system are as follows. At the beginning of the emulsification, the major compositions of the system were oil (TGDDM or modified TGDDM) and small amount of emulsifiers. Meanwhile, deionized water was guttatim added into the system. At the moment, the oil was predominant and wrapped the water drop, which was water-in-oil. Then, with the increase in water content, water droplets aggregated and turned into continuous phase under the shear strength. Last, the oil dispersed as the micelles into the water, which was oil-in-water and the stable emulsion was obtained by the emulsification of the emulsifiers. After the phase transformed completely, the speed of water dropping was increased to 7 mLmin^{-1}. Last, an emulsion containing approximate 20% by weight of the solid component was successfully obtained.

Sizing Treatment of CF
As the CF T700 SC was commercial sized, the sizing layer coated on the CF should be removed. CF T700 SC was refluxed with acetone in a Soxhlet apparatus for 36 h. CF was then washed repeatedly with deionized water and dried in a vacuum oven at 100°C for 2 h. The self-made sizing agent was diluted

Table I. Compositions of Modified TGDDM

Modified resin	MR1	MR2	MR3	MR4	MR5
TGDDM/ dodecylamine reaction mass ratio	80 : 20	85 : 15	90 : 10	95 : 5	100 : 0
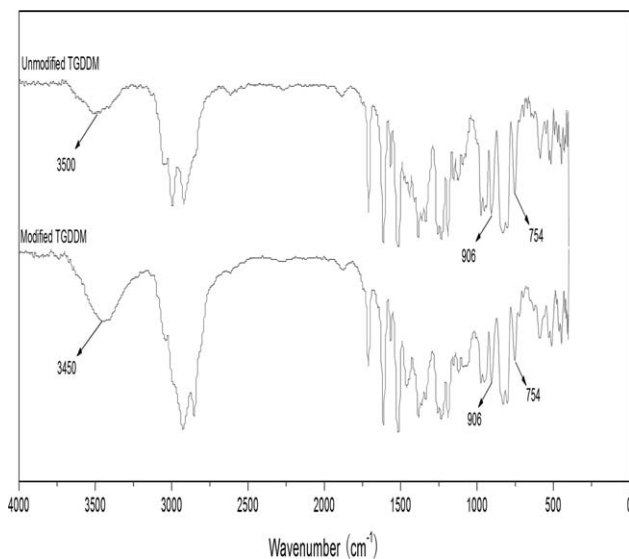
Figure 2. FTIR of the modified TGDDM (MR1) and unmodified TGDDM.

with deionized water to obtain an emulsion with 0.5% solid component. Dipping method was used in the sizing treatment process, that is, the desized CF was immersed in the sizing agent for 30 s by use of a dip tank in conjunction with automatic processing equipment for continuous pulling the CF through the dip tank. CF was then dried at 100°C for 20 min.[24]

Composite Preparation

Vacuum bag molding technology was used in the composite preparation process. The matrix resin was TGDDM, and the curing agent was DDS. The mass ratio of TGDDM to DDS was 100 : 40. The curing agent was slowly added into the resin with a continuous stirring over 15 min. The mixture was pumped through the pipe to sufficiently infiltrate the CF fixed on the mold which was wrapped with a vacuum bag. Then, the subsequent curing process was listed as follows: 100°C for 1 h, 1 h at 120°C, 2 h at 140°C, 2 h at 160°C and 2 h at 180°C, with post-curing for 2 h at 200°C.

Characterization

Particle Size of the Sizing Agent. Particle size and distribution of sizing agents were analyzed by a LS-13320 laser particle size analyzer (Beckman Coulter.,) using the polarization intensity differential scattering technology (PIDS) at 25°C. The mean diameter of the particles was determined by the software provided by Beckman Coulter instrument.

Chemical Structure and Composition of the Modified TGDDM. The chemical structure and composition of the modified resin were investigated by a nicolet 380 infrared spectrometer (Thermo Electron Corp.,) using the transmittance method with a spectral range from 4000 to 400 cm^{-1} at a resolution of 5 cm^{-1}. The specimens were prepared through the liquid-film method, that is, the resin was dropped between two KBr salt films to form liquid film.

Thermostability of Sizing Agent. The major functional composition of sizing agent is film former (in this test, the film former resins were E-44, TGDDM and modified TGDDM epoxy resin),

which will participate in the subsequent curing reaction and chemically bond with the matrix epoxy resin. Herein, the heat resistance of the sizing agent is the thermostability of the cured resin in nature. The curing process of the epoxy resin was the same with that of Composite Preparation section, and the dosage of the curing agent DDS was according to the actual equivalents of epoxy groups in different epoxy resins. By DSC test, the glass transition temperatures (T_g) of different cured film former resins could be obtained. The DSC tests were carried out on a STA409EP thermal analyzer (NETZSCH, Germany) with the testing temperature ranged from 50°C to 400°C at a heating rate of 5°C min^{-1} in a nitrogen gas flow.
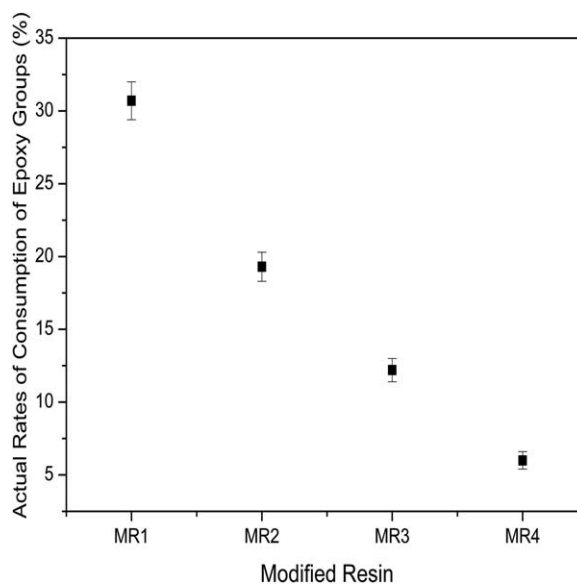
Rate of Consumption of Epoxy Groups. Hydrochloric acid/acetone method (GB 1677-81) was utilized to measure the epoxy values of pure TGDDM and modified TGDDM. Rate of consumption of epoxy groups ($\varepsilon\%$) was obtained by eq. (1).

$$\varepsilon\% = (E_0 - E_j)/E_0 \times 100\% \tag{1}$$

where E_0 and E_j refer to epoxy value of the pure TGDDM and modified TGDDM, respectively. The results were averaged from five successful measurements.

CF Surface Morphology. The surface morphology of the sized and desized CF was observed by a FEI QUANTA FEG250 type SEM (FEI.,) with an accelerating voltage of 10 kV. Before the test, specimens were sputter coated by Au with several nanometers thick to make them electrically conduct.

Abrasion Resistance of CF. Abrasion resistance of CF was measured by a textile abrasion tester produced by Shandong Textile Academy (China). Diameters of the stainless steel rod and the guide rollers were 15 mm and 10 mm, respectively. The angle between the stainless steel rod and two guide rollers was 120°. CF was rubbed by the abrasive paper on the stainless steel rod repeatedly with a load of 200 g at a constant rate of 120 rmin^{-1}. When the CF fractured, abrasion resistance times on

Figure 3. Actual rates of consumption of epoxy groups.
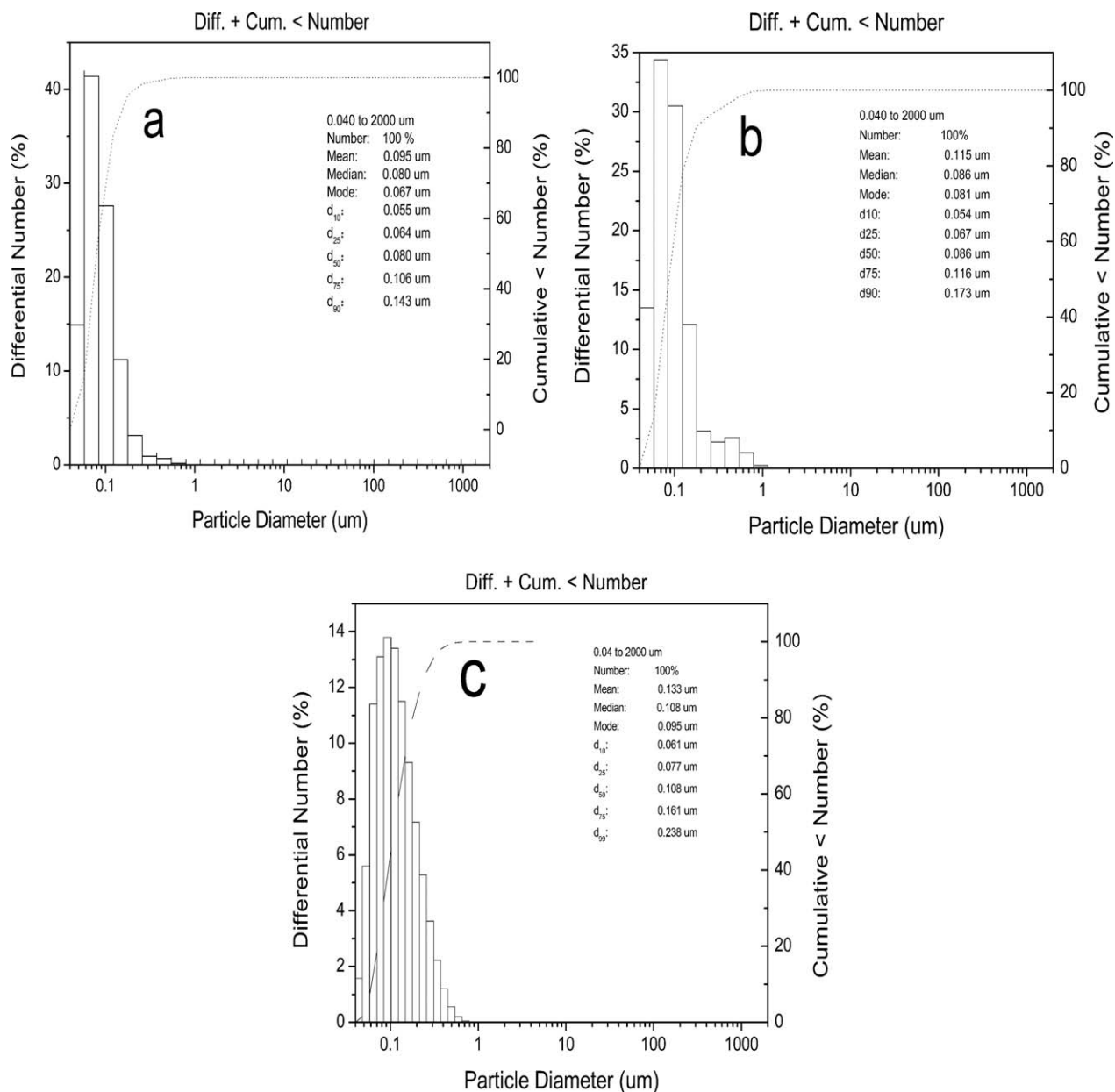
Figure 4. Particle size and distribution of sizing agents: (a) SA5, (b) SA3, and (c) SA1.

the monitor were recorded. Five CF bundles were measured, and the average value of abrasion resistance times was obtained.

Fluffs of CF. Fluffs were measured according to a Japanese patent.[27] CF was dragged through polyurethane sponges (5 × 10 × 40 mm) at the rate of 1 mmin^{-1}. The weight of fluffs on the sponges was recorded 10 min later. Five CF bundles were measured, and the average value was obtained.

Stiffness Measurement. According to ISO 3375-2009, the stiffness of CF was measured. The center of the CF bundle whose length was 500 mm was hung on a stainless steel hook (radius = 10 mm). The distance between the two hanging terminals of the CF was measured with a slide gauge 30 s later. Five CF bundles were measured and the average value was recorded.

ILSS of CF/TGDDM Composites. ILSS of composites was measured according to ASTM D-2344 which was a three-point, short-beam shear method. The dimensions of specimen were 20 × 6 × 2 mm, and the length of span was five times as many as the depth of the specimen. Thereafter, specimen was tested by a WDW-30-type universal testing machine (Shanghai Shengli Company, China). The speed of the crosshead was 1 mmmin^{-1}, and the failure load on the monitor was recorded when the spacemen broken. Ten specimens were measured, and the ILSS values of the composites were calculated according to the eq. (2).

$$ILSS = 3P/4hb \qquad (2)$$

where P is the maximum compression load at fracture in Newtons (N), h and b are the thickness and width of the specimen in mm, respectively.
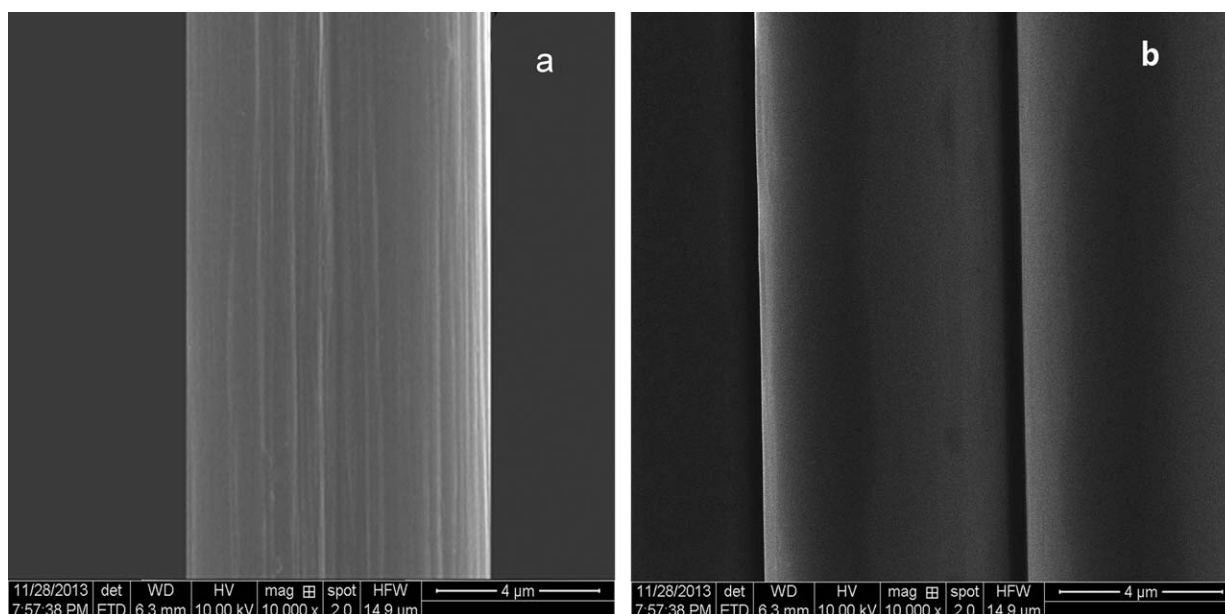
Figure 5. SEM images of (a) desized CF and (b) sized CF.

RESULTS AND DISCUSSIONS

Chemical Structure of the Modified TGDDM and Rate of Consumption of Epoxy Groups

The FTIR spectra of the modified TGDDM (MR1) and unmodified TGDDM are revealed in Figure 2. In the spectrum of the unmodified TGDDM, 3500 cm^{-1} is the absorption peak of the hydroxyl group. Due to the reaction between dodecylamine and TGDDM, a few of epoxy groups participated in the ring-opening reaction, generating a number of hydroxyl groups. Accordingly, the absorption peak of the hydroxyl group at 3450 cm^{-1} of the modified resin spectrum turns deeper. This reaction also leads to the decrease in the absorption peak of the epoxide group at 754 cm^{-1} and 906 cm^{-1} in the modified resin spectrum. Moreover, the absorption peaks that were related with the primary amine and secondary amine (N-H) stretching vibration range from 3250 cm^{-1} to 3400 cm^{-1}. Nevertheless, as judge from the spectrum of the modified TGDDM, the peaks of them are not existent. This indicates that the amidogens reacted adequately and tertiary amine generated.

The actual rates of consumption of epoxy groups of modified resin with different reaction mass ratio of dodecylamine/TGDDM are revealed in Figure 3 (error bars indicate standard deviation). As it is clearly observed, the higher the content of dodecylamine, the more epoxy groups react. The actual rates of consumption of epoxy groups are 30.7%, 19.3%, 12.2%, and 6.0%, when the resins are MR1, MR2, MR3, and MR4, respectively (The theoretical rates of consumption of epoxy groups are 32.3%, 20.1%, 12.6%, and 6.2%, respectively). Herein, the epoxy groups participating in the reaction are close to the theoretical value. All the results verify the reaction between dodecylamine and TGDDM.

Stability of Sizing Agent

All the self-made sizing agents could maintain no precipitation after three months, which showed a great potential for practical industrial application. To make further investigation on the stability of the sizing agents, particle sizes and distributions of the sizing agents were tested and listed in Figure 4.

As shown in Figure 4, the mean particle sizes of different sizing agents range from 95 nm to 133 nm. The result also indicates that the mean particle size increases with the dodecylamine content of sizing agent increasing. Due to the reaction between TGDDM and dodecylamine, the structure of the resin was changed. This might have a slight effect on the emulsion preparation process.[28] The particle sizes (on a nanoscale) of all the sizing agents distribute uniformly and narrowly. These two aspects reveal good stabilities of the sizing agents according to the Stoke Law.[20]

Table II. Tests of Handling CF

Specimen	SA1 handling CF	SA2 handling CF	SA3 handling CF	SA4 handling CF	SA5 handling CF	Desized CF	T700 SC CF
Abrasion resistance (time)	1765 ± 103	1697 ± 94	1621 ± 109	1577 ± 128	1519 ± 115	647 ± 58	1296 ± 96
Stiffness (mm)	63 ± 3	66 ± 1	66 ± 2	68 ± 3	75 ± 2	21 ± 2	61 ± 3
Hairiness (mg)	3.9 ± 0.2	4.1 ± 0.3	4.5 ± 0.1	4.9 ± 0.3	5.2 ± 0.2	13.8 ± 0.3	3.5 ± 0.1

The critical factors concerning preparing a stable emulsion include that the selection and dosage of emulsifiers combined with stirring rate and emulsifying temperature.[29] By referring to literatures[28–31] and the previous experiments in laboratory, the best experimental scheme was carried out. The mass ratio of resin and the mixed emulsifier was 10 : 1. The emulsifier was an NP-10/1601 mixture of 1 : 1 by mass. The emulsifying temperature was 50°C. The stirring rate was 11000 rmin^{-1}.

Synthetically, the particle sizes and distributions of the emulsions indicate that the stable sizing agents were prepared.

Morphology of Sized and Desized CFs

The surface morphology images of the desized CF and the sized CF are revealed in Figure 5.

SEM images demonstrate the obvious difference between the (a) desized CF and the (b) sized CF. There are some concaves and defects on the surface of the desized CF, resulting from the spinning technique during the manufacture process of CF. However, as shown in Figure 5(b), when CF was sized by the sizing agent (SA1), the surface of CF was relatively smooth. The uniform sizing layer assists in weakening stress concentration in the flaw. It can also help the CF yarns obtain adequate convergence and superior handleability. Accordingly, CF is protected from the fuzzing and fragmenting.[32] Moreover, if the chemical composition of the sizing layer on the surface of CF is same or similar to matrix resin, it will be beneficial to improve the adhesion between the CF and the surrounding resin.[33]

Influence of Sizing Agent on Handleability of CF

The results (mean ± standard deviation) of abrasion resistance, fabric hairiness, and stiffness tests are demonstrated in Table II. As judged from Table II, the sizing agent treatment can not only dramatically enhance the abrasion resistance of CF, but also decrease the weight of fluffs and breakage. Compared with that of the desized CF (13.8 mg), the minimum value of fabric hairiness weight of CF (sized with SA1) is only 3.9 mg which is close to that of Japan commercial T700 CF (3.5 mg). Abrasion resistances of the sized CF range from 1519 times to 1765 times. It is significantly superior to the abrasion resistance of the desized one (647 times) and also much higher than that of T700 CF (1296 times). Meanwhile, the stiffness values of all the handling CFs are little differences. However, if we take a closer look in Table II, it is revealed that the higher the content of dodecylamine is in sizing agents, the slightly lower the stiffness of the sized CF is. Moreover, as the mass ratio of dodecylamine increases, the abrasion resistance of the sized CF enhances.

The rigid benzenes in TGDDM molecule make the resin less flexible and more brittle. Therefore, the unmodified TGDDM sizing film is inflexible and easy to fracture under the friction and blending force during CF-weaving process. Nevertheless, because of the reaction between TGDDM and dodecylamine, flexible aliphatic chains ($-C_{12}H_{25}$) were inserted into TGDDM. The aliphatic chains were connected with single bonds that could easily internally rotate.[34] Simultaneously, self-cross-linking of TGDDM was also weakened.[35] These two factors were beneficial to improve the toughness of the resin. When a stress acted on the cured modified resin, cracks would occur and then spread from the crack tip. The flexible chains could availably retard the crack extension for its function of alleviating stress and form a stress relaxation area, which could make plastic deformation happen. Accordingly, the brittleness of the resin was decreased. With the content of dodecylamine increasing, the properties of the modified resin, such as toughness, resilience, and draftability were improved. Therefore, when CF was coated by the modified TGDDM emulsion sizing agent, the abrasion resistance of the CF was boosted.[36]

It is known that bending force and friction act on CF frequently during the spinning process. CF without surface protection will be cracked easily. The broken fluffs turn to be wool balls under the friction and shear force. Unfortunately, the wool balls rub the other fibers that will accelerate the break of fiber bundle. Due to the excellent adhesion force between sizing agents and CF, sizing agents are able to cluster the dispersive CF. In addition, a uniform layer on the surface of CF can effectively prevent CF from abrasion. Herein, CF sized with a sizing layer has a low value of fluffs.

Toughness of CF is intuitively reflected by the test result of stiffness. As revealed in Table II, stiffness of the sized CF ranges from 63 to 75 mm, which is a slightly higher than that of T700 CF (61 mm), whereas the desized one is 21 mm.

During CF-weaving process, CF is blended to a wide angle and suffered from flexural stress. An appropriate stiffness of CF is suitable for the specific textile technology. Accordingly, the stiffness of CF could be changed by means of adjusting the ratio of the TGDDM and dodecylamine to adapt to different manufacturing techniques.

The stiffness of CF coated with SA5 was 75 mm, which was slightly greater than that of CF sized by SA1, SA2, SA3, or SA4. The reason was the pure TGDDM-sizing film made the CF stiff
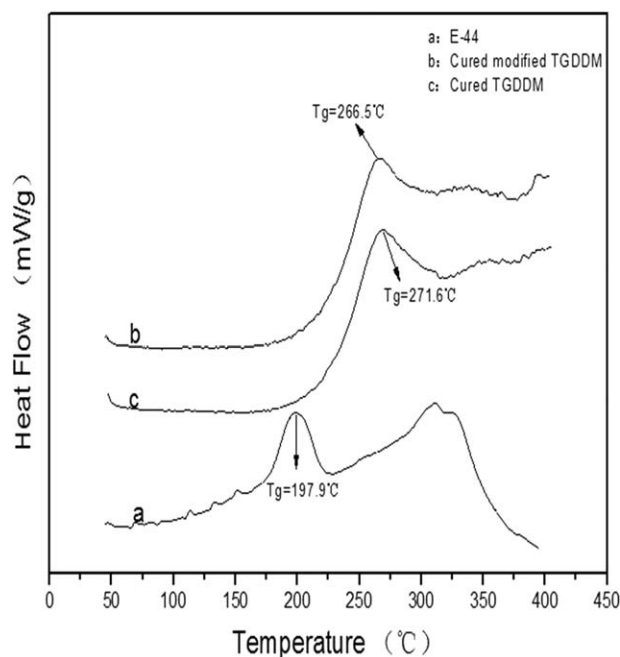

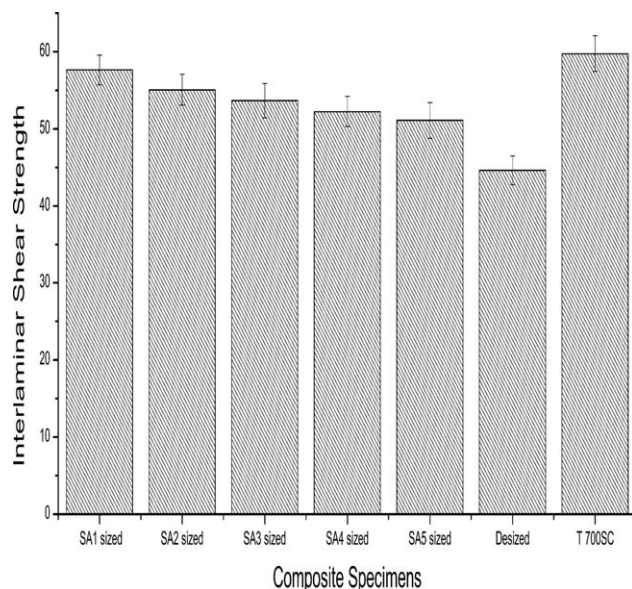**Figure 6.** DSC curve of the cured epoxy resin.

Figure 7. ILSS of CF/TGDDM composites.

and less ductility. When the flexible chain ($-C_{12}H_{25}$) was inserted, the toughness of the sizing agent was improved.

Thermostability Test of Sizing Agent
As shown in Figure 6, the T_g of the cured pure TGDDM is 271.6°C, which is slightly higher than the T_g of the modified TGDDM (MR1) (266.5°C), whereas the T_g of the cured E-44 is only 197.9°C.

Due to the reaction between dodecylamine and TGDDM, some saturated aliphatic chains were inserted into the resin. Although these single bonds chains that are easy to internally rotate and motion under the attack of high temperature lower the T_g of the modified resin, it is still much higher than the T_g of E-44 epoxy resin. This attributes to the high-cross-linking and rigid structure of the cured TGDDM. Moreover, the selection of the

curing agent was in light of the Ref. 37, which demonstrated that DDS is one of the most important epoxy resin hardener that can make the cured epoxy resin obtain superior properties for both mechanics and heat resistance. Accordingly, the heat resistance of the modified TGDDM-type sizing agent is excellent and much superior to that of the general epoxy resin.

ILSS of CF/TGDDM Composites
Interfacial adhesion between CF and matrix resin was evaluated by ILSS measurement. The comparison of ILSS data (error bars indicate the standard deviation) of composites based on the CF treated with different sizing agents is shown in Figure 7.

Figure 7 indicates that ILSS value improves apparently after CF was coated by sizing agent. ILSS of the composite based on the CF sized with sizing agent SA1 reaches maximum value of 57.63 MPa, which is slightly lower the T700 SC CF composite (59.75 MPa), increasing by 29.16% compared with the composite with the desized CF (44.62 MPa). It has been proved that the loads can be effectively transformed from resin to CF.[38] The chemical bonding forces and Van der Waals forces are found among the molecules and mechanical anchor forces between CFs and matrix. The chemical bonding forces play the leading role in the adhesion between CFs and matrix resin, while the others are subordinate,[39] because the major component of the sizing agent is chemically same to matrix resin, the sizing layer on the CF surface is beneficial to improving the fibers wetting by matrix resin.[40] Moreover, many epoxide groups in the sizing agent layer on the CF surface are able to take part in the subsequent curing reaction and solidly cross-link with the matrix resin together. Synthetically, sizing treatment can greatly enhance the interfacial adhesion between the CF and matrix resin.

As revealed in Figure 7, higher the mass ratio of dodecylamine in the sizing agent, higher the ILSS of the composite obtained. There are two aspects to explain the above result. For one reason, hydroxyl
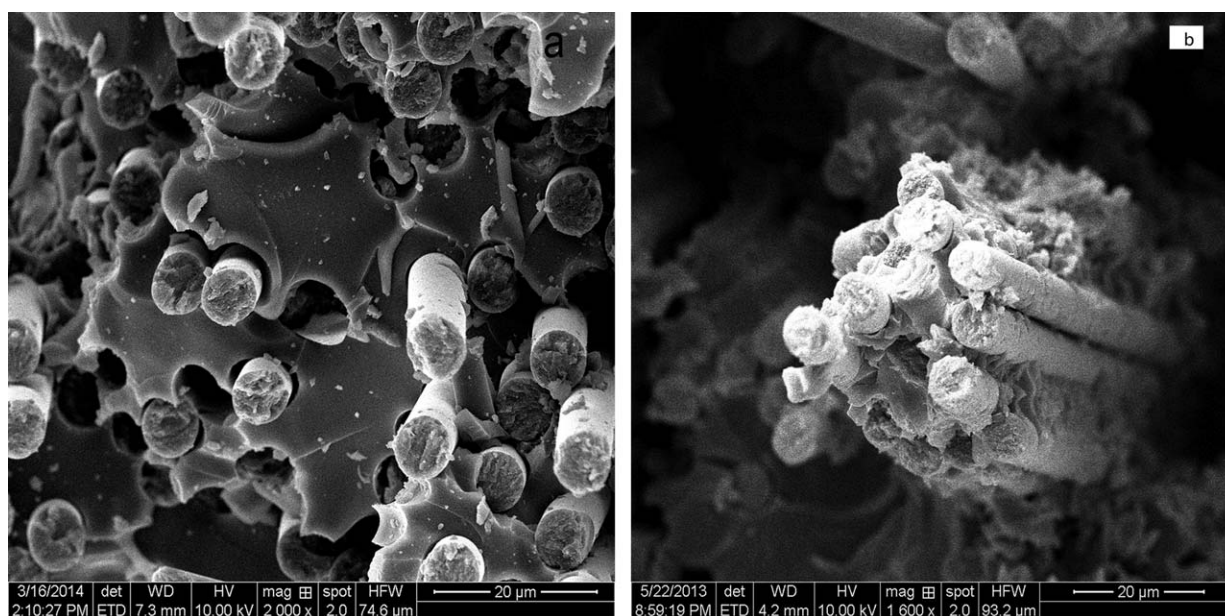

Figure 8. Fracture surface of the composites based on desized CF (a) and SA1-sized CF (b).

groups were introduced into the modified TGDDM (the film former), when the reaction between dodecylamine and TGDDM occurred. More the dodecylamine participated in the reaction, more the hydroxyl groups generated. It is well known that the introduced hydroxyl radicals is able to increase surface energy of the fiber, and then, CF with a high surface energy is easy to infiltrate.[41] The other reason plays a leading role in enhancing the interfacial bonding. With the flexible aliphatic chains ($-C_{12}H_{25}$) introduced into TGDDM, the epoxide equivalent of modified TGDDM was less than that of unmodified one. This means that the distance between two adjacent epoxy groups in modified TGDDM was larger than that of unmodified one. Accordingly, the cross-linking density decreased when the modified TGDDM on the surface of CF participated in the curing process. Flexible aliphatic chains interspersing in the highly cross-linked TGDDM network contributed to forming the nonuniform continuous phase and plastic deformation.[37] In addition, the flexible aliphatic chains in the cross-linking network could adequately disperse and absorb the external force when a load acted on the interface, because the single bond chains ($-C_{12}H_{25}$) were able to internally rotate. Herein, a flexible interface between CF and matrix resin was formed by inserting the long flexible aliphatic chains into TGDDM.[42]

SEM images of the fracture surface of the composites with SA1-sized CF and the desized CF are demonstrated in Figure 8.

Figure 8(a) reveals that the desized CF is thoroughly divorced from the matrix resin with little resin cohering on the fractured CF surface for the weak bonding strength between them. Meanwhile, there were numerous holes on the fracture surface due to the debonding CFs. Accordingly, the interfacial adhesion between the matrix resin and fiber is poor. However, as shown in Figure 8(b), there is abundant resin remained on the sized CF surface. It is intuitively proved that the interfacial bonding between the CF and matrix resin drastically improved after the fiber was sized. This is due to the enhanced interfacial compatibility and chemical interaction.

CONCLUSIONS

TGDDM and dodecylamine were reacted at mass ratios of 80 : 20, 85 : 15, 90 : 10, and 95 : 5, respectively. The modified resins were used as the film formers of the sizing agents. CF obtained a better handleability after sized with self-made sizing agents. When TGDDM reacted with dodecylamine at a mass ratio of 80 : 20, the best synthetical properties of the sizing agent (SA1) obtained. The abrasion resistance of SA1-sized CF was 1765 times. The fabric hairiness weight was 3.9 mg. ILSS of SA1-sized CF composite obtain the maximum value of 57.63 MPa, increasing by 29.16% and 12.8%, compared with the desized CF and SA5 (unmodified TGDDM-sizing agent)-sized CF composite, respectively. Moreover, the heat resistance of TGDDM-type sizing agent made in this work was much superior to the general epoxy resin (E-44)-type sizing agent.

ACKNOWLEDGMENTS

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