# Reaction of carbon fiber sizing and its influence on the interphase region of composites

**Qing Wu, Min Li, Yizhuo Gu, Shaokai Wang, Xingxing Wang, Zuoguang Zhang**
Key Laboratory of Aerospace Materials and Performance, Ministry of Education, School of Materials Science and Engineering, Beihang University, Beijing 100191, China
Correspondence to: M. Li (E-mail: leemy@buaa.edu.cn)

**ABSTRACT:** What might happen with the interphase region of composite if the sizing agent cannot afford the attack of processing temperature and firstly reacted before its combination with the resin, is rarely reported. On the basis of this, herein, effects of sizing reaction on the interphase region of composite were investigated, as well as on the carbon fiber surface properties. It showed that the interfacial shear strength of carbon fiber/epoxy composite was improved after the sizing reaction. The interphase modulus was also increased with a thinner gradient distance. Further analysis indicated that the fiber surface roughness increased, the fiber wettability with the resin lowered, and the chemical reactions between sizing agent and resin reduced after 200°C/2 h treatment on carbon fiber. These results explained the change of the interphase region, which are meaningful for sizing optimization. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41917.

## INTRODUCTION

Temperature resistant property of polymer matrix composites is essential for aerospace and aircraft applications, because it determines the reliability and safety of composite structures during long exposures at use temperature as high as 371°C.[1,2] Apart from polymer matrix,[3–5] the temperature resistance of composites greatly depends on the fiber-matrix interphase.[6]

The interfacial properties relate with the chemical composition and morphology of carbon fiber surface, as well as the wettability and interactions between fiber and matrix, which can be tailored by the sizing coat of the carbon fiber.[7–9] Weitzsacker et al.[10] showed that composite processing at temperature above 300°C resulted in the removal of surface oxygen and the available reactive sites on fiber surface. Liu et al.[11] indicated that interfacial heat resistance depended on the interaction of sizing agent with matrix and the chain motion of the interphase cross-link structure. Therefore, high thermal stability and durability are desirable for a good sizing agent. So far, temperature-resistant types of sizing agents were reported as up to 300°C, such as phenylethynyl-terminated imide oligomers (LARC PETI-5®),[12,13] polysulfone or polyphenylene sulfide,[14] poly(phthalazinone ether ketone),[15] and mixture of polyimide GCPI[TM] and epoxy 618.[16] However, these sizing agents are not appropriate for widely used carbon fiber composites due to the lower compatibility with epoxy resin. For commercial availabil-

ity, sizing agents are mostly epoxy type because of its good similarity with the generally used epoxy matrix.

Our previous works showed that the sizing agent (epoxy type) has chemical reactivity, which helps to improve the adhesion between carbon fiber and epoxy matrix.[17–19] However, what might happen with carbon fiber surface and the interphase region, if the sizing agent cannot afford the attack of processing temperature and firstly reacted before its combination with resin, is rarely reported.

The objective of this work is to study the effects of sizing reaction on the interphase region of carbon fiber/epoxy composites, such as adhesion, modulus, and thickness. To achieve this objective, an understanding of the physicochemical changes on carbon fiber surface and the variation of chemical reactions between sizing agent and epoxy matrix is needed. To obtain carbon fiber with reacted sizing layer, 200°C heat-treatment for 2 h was conducted on the carbon fibers. Storage modulus and the thickness of interphase region were analyzed using dynamic nanomechanical mapping method. Interfacial shear strength (IFSS) of composite was investigated by micro-droplet test. The fiber surface roughness and the chemical properties before and after 200°C heat-treatment on fiber were characterized by Atomic force microscope (AFM) and X-ray photoelectron spectroscopy (XPS), respectively. The wettability of fiber with resin was investigated by contact angle measurement. Moreover,

**Table I.** Performance Parameters of Carbon Fiber and EP Matrix

| Parameters | CF1 | CF2 | EP |
|---|---|---|---|
| Tensile strength (MPa) | 5460 | 5900 | 86 |
| Tensile modulus (GPa) | 294 | 294 | 3.5 |
| Elongation (%) | 1.9 | 2 | 3.4 |
| Density (g/cm$^3$) | 1.8 | 1.8 | 1.26 |
| Fiber diameter ($\mu$m) | 5.5 | 5.5 | – |
| Sizing content (%) | 1.34 | 0.51 | – |

chemical reactions between sizing and resin matrix before and after sizing reaction were analyzed by fourier transform infrared spectroscopy (FTIR).

## EXPERIMENTAL

### Materials
Two sized T800 grade carbon fibers (Toray), respectively marked as CF1 and CF2, were used. A high-temperature cured epoxy 5228 matrix (EP for short) with standard curing cycle of 130°C 1 h + 180°C 2 h + 190°C 3 h was supplied by Beijing Institute of Aeronautical Materials. The properties of carbon fiber and EP matrix are summarized in Table I.

Soxhlet method was used to extract the sizing agents from CF1 and CF2 surfaces, which was conducted with acetone at 80°C for 24 h with about 20 m fiber in length. The extracted sizing content was evaluated by the mass difference between the original sized carbon fiber and the desized carbon fiber, divided by the original sized fiber mass. The sizing agents completely extracted from CF1 and CF2 were designated as CF1-sizing and CF2-sizing, respectively, and the fibers after sizing removal were marked as desized-CF1 and desized-CF2.

### Processing Condition
Our previous research results showed that chemical reactions could take place in sizing at 200°C/2 h heat-treatment.[18,19] Moreover, most thermosets, e.g., epoxy and bismaleimide resin matrices, are cured and post cured at temperature around

200°C, which inevitably impact the chemical reactions of the sizing agent itself and the reactions between the sizing and the resin matrix, and hence influence distribution of the outcome crosslinks in the interphase region of those composites. Therefore, 200°C/2 h heat-treatment was conducted on carbon fiber and on the extracted sizing agent as well. Carbon fibers after 200°C treatment were marked as heat treated-CF1 and heat treated-CF2, respectively. CF1-sizing and CF2-sizing after 200°C treatment were designated as CF1-sizing-heat treated and CF2-sizing-heat treated. The extracted sizing agents from heat treated carbon fibers were named as heat treated-CF1-sizing and heat treated-CF2-sizing, respectively. Correspondingly, the heat treated carbon fibers after sizing removal were labeled as desized-heat treated-CF1 and desized-heat treated-CF2.

Figure 1 shows the FTIR spectra of the sizing agents before and after 200°C/2 h heat-treatment. According to the changes in spectral peaks, the composition of CF1-sizing is much different from that of CF2-sizing, but the typical vibration peaks at around 1250, 930, and 830 cm$^{-1}$ of epoxide group indicate that they both contain epoxy constituent. Spectrum bands of CF1-sizing at 3391 and 3320 cm$^{-1}$ arise from N—H stretching, which also cover the —OH band. C=O vibration at 1713 cm$^{-1}$ should be from ketone unit. Functional groups in CF2-sizing at 3386.4, 1724.5, and 1105.9 cm$^{-1}$ are respectively ascribed to group vibrations of hydroxyl, carboxyl and C—O of secondary alcohol or allyl tertiary alcohol. After 200°C/2 h treatment, the vanishing of N—H group, the increase of hydroxyl group and the decrease of epoxide group show the occurring of chemical reactions in CF1-sizing. Similarly, the decrease peak intensities of hydroxyl, carboxyl, and epoxide groups also indicate the chemical reactions of CF2-sizing.

### Characterization
**Interfacial Shear Strength of Carbon Fiber/Resin Composite.** Micro-debonding was used to evaluate the IFSS of carbon fiber/EP composites on MODEL HM410 device (Japan's East Wing Industrial) with moving speed of 0.03 mm/min at the sensitivity of 1/100 gf. The resin matrix was wetted onto a single fiber to
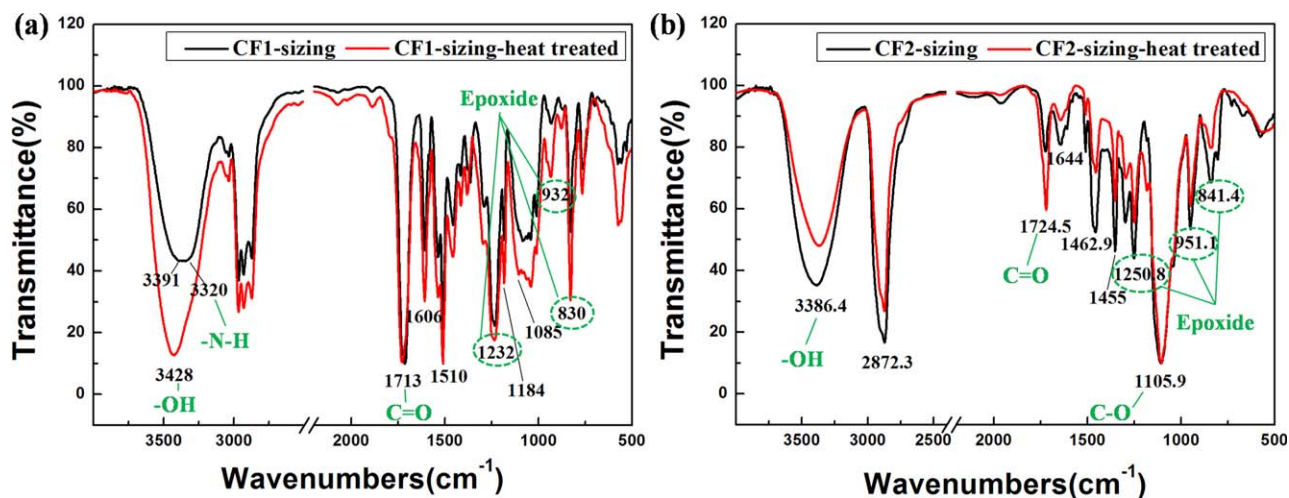


**Figure 1.** FTIR spectra of the sizing agents before and after 200°C treatment for 2 h: (a) CF1-sizing, (b) CF2-sizing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

form a micro-droplet surrounding the fiber, which was then cured in an oven. After cure, the single fiber was fixed on a concave frame. The knives came in contact with the solid resin droplet and the force required to debond the droplet from the fiber was recorded. The embedded length of each micro-droplet was measured through optical microscopic observation. IFSS was calculated using the equation:

$$\tau_{IFSS} = \frac{F}{\pi dl} \qquad (1)$$

where $\tau_{IFSS}$ is IFSS, $F$ is the maximal load, $d$ is the diameter of the fiber, and $l$ is the embedded length of the resin droplet. Each reported IFSS value is the average of 15 valid data.

**Interphase Modulus and Thickness Analysis.** Interphase thickness of carbon fiber/epoxy composite was measured based on the statistical data of the storage modulus obtained by dynamic nanomechanical mapping method, using a nanomechanical testing instrument (Hysitron, TriboIndenter). The prepared samples were indented with a diamond tip (Berkovich probe of 50 nm radius) by superimposing a dynamic force of 1 $\mu$N at 200 Hz upon a constant normal force of 2 $\mu$N. The low indentation force resulted in the low penetration depth (of 1–3 nm) in interphase and resin matrix regions, and the region affected by the tip is calculated to be 10–17 nm. Scanning region is 10 $\times$ 10 $\mu m^2$ at the cross-section around a carbon fiber with 256 $\times$ 256 pixels of resolution. The parameter setting is able to eliminate the effects of residual stress and plastic deformation from neighboring indents.

The interphase region is generally believed to have different mechanical properties from those of the fiber and the resin.[20,21] Thus, the profile of pixel counts as a function of the natural logarithm of storage moduli (65,536 data points) is plotted. The pattern of interphase was obtained by excluding the moduli that belong to the fiber and the matrix regions, and further the quantitative dimension of interphase was calculated.

Further details of the sample preparation and the testing procedure were referred to our previous work.[22]

**Morphology and Surface Roughness of Carbon Fiber.** Surface morphology and roughness analysis were determined by Veeco-Dimension icon AFM with a scanning region of 3 $\times$ 3 $\mu m^2$. For each type of carbon fiber, at least 20 different locations were probed. NanoScope Analysis software was used to calculate the fiber surface roughness (Ra). Each reported Ra of carbon fiber was an average value of at least 20 valid data.

**Surface Chemical Property of Carbon Fiber.** The surface chemistry of carbon fiber was performed by XPS (ESCALAB 250, ThermoFisher Scientific) with a monochromatic Al K$\alpha$ X-ray source at 200 W. The pass energy was fixed at 200 eV for survey and 30 eV for high resolution scans with spot size of 500 $\mu$m for the analyses. Peak binding energies were calibrated upon C1s peak at 284.8 eV. A six-parameter curve fitting was made for the C1s spectra using XPSPEAK software.

**Contact Angle Between Carbon Fiber and Resin.** Advancing contact angles between resin and single fibers were measured using a dynamic contact angle and surface/interfacial tension

instrument (DCAT21, Dataphysics), according to modified Wilhelmy method. All the contact angles were obtained at 80°C with an immersion speed of 0.01 mm/s, surface detection threshold of 0.15 mg and immersion depth of 3 mm. Thirty single carbon fibers were tested to get an average value.

**Chemical Reaction Analysis.** Nicolet Nexus 470 FTIR was applied to evaluate the functional groups in the mixtures of sizing/resin. Considering that chemical reaction is hard to be *in situ* detected at carbon fiber surface, thus the extracted sizing agent was artificially mixed with equal volume EP to mimic the real situation. The mixture was dispersed in KBr powder with a mass ratio of 1 : 100–1 : 200, and spectra were obtained in an optical range of 400–4000 cm$^{-1}$. Chemical interaction was estimated by concentration differences of the functional groups before and after 200°C/2 h treatment. 180°C/2 h treatment was conducted on sizing/EP mixture according to the aforementioned curing cycle of EP. The peak at 1610 cm$^{-1}$, which is assigned to the vibration of benzene ring, was selected as the reference peak. The relative concentration of typical functional group was calculated by the following equation:

$$C_x = \frac{I_x}{I_{reference}} \qquad (2)$$

where $C_x$ is the concentration of $x$ group, $I_x$ is the peak height of $x$, and $I_{reference}$ is the height of reference peak (benzene ring at 1610 cm$^{-1}$).

## RESULTS AND DISCUSSION

### Influence of Heat-Treatment on Interfacial Properties of Carbon Fiber Composites

We first examined the IFSS of the carbon fibers before and after 200°C/2 h heat-treatment with EP matrix, as shown in Figure 2. IFSS of CF1/EP is 77 MPa, lower than 85 MPa of heat treated-CF1/EP. Similarly, IFSS of CF2/EP (79 MPa) is lower than that of 88 MPa for heat treated-CF2/EP. This indicates that the interfacial adhesion is improved after 200°C treatment on carbon fiber.
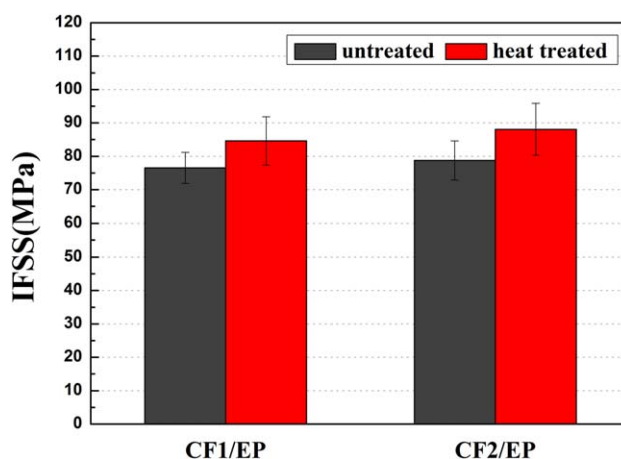


**Figure 2.** IFSS of carbon fiber before and after 200°C/2 h treatment with EP resin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
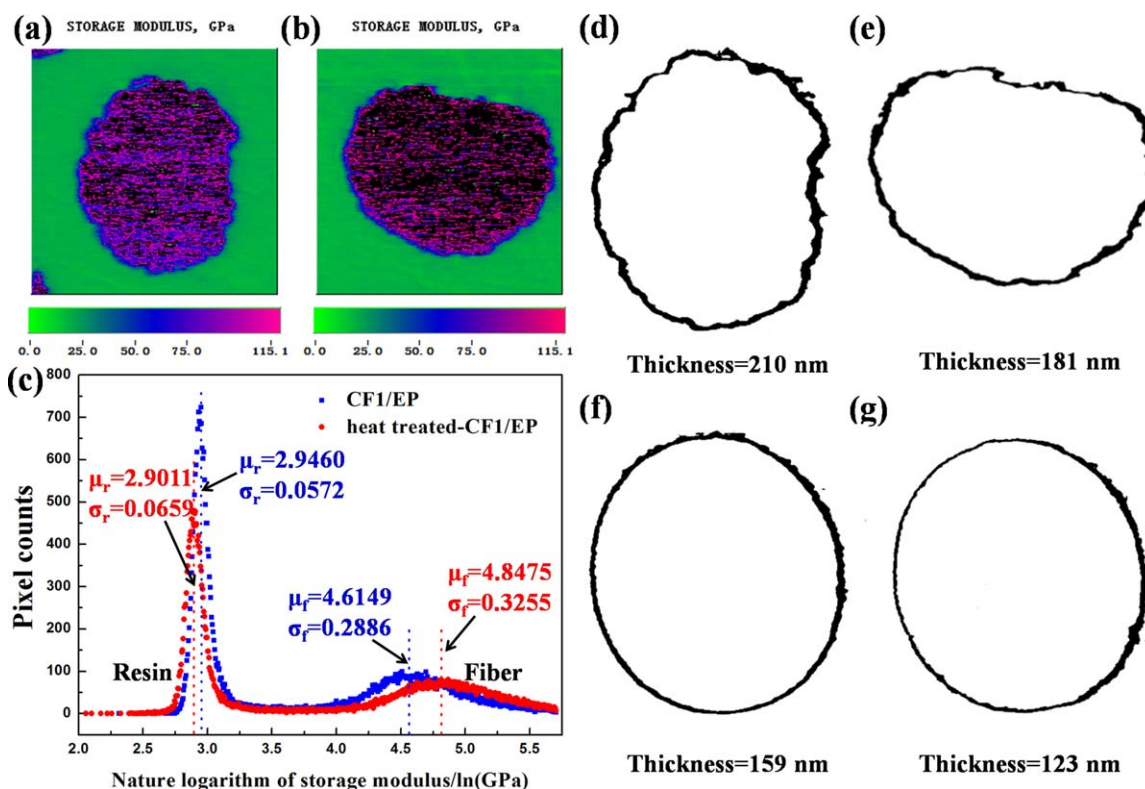
**Figure 3.** The storage modulus of composite with an area of $10 \times 10 \ \mu m^2$: (a) CF1/EP, (b) heat treated-CF1/EP. (c) Histogram of the data of storage modulus image in Figures 3(a,b), where the narrow and wide distributions correspond to resin and fiber regions, respectively. The interphase dimension of: (d) CF1/EP, (e) heat treated-CF1/EP, (f) CF2/EP, (g) heat treated-CF2/EP, which is extracted by excluding the moduli that belong to the fiber and the matrix regions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Since storage modulus is very sensitive to changes of molecular structure and mobility taking place in the fiber-matrix interphase,[23] dynamic mechanical mapping was adopted to determine the changes of interphase storage modulus and thickness before and after 200°C heat-treatment on carbon fiber. The results are depicted in Figure 3. Figure 3(a,b) are storage modulus maps of CF1/EP and heat treated-CF1/EP composites, respectively. It clearly shows that the carbon fiber has the highest storage modulus followed by the intermediate region existing in the vicinity of the fiber. The EP matrix exhibits the lowest storage modulus. To obtain the information of the entire interphase, the profile of the pixel counts as a function of the natural logarithm of storage moduli is plotted in Figure 3(c). The narrow and wide peaks correspond to resin and fiber regions, respectively. $\mu$ and $\sigma$ are mean and standard deviation, respectively of the natural logarithm of the storage moduli for the two regions, which are calculated by peak fitting using a lognormal distribution. According to the statistical analysis, the interphase is defined as the region where the natural logarithm of the storage modulus ranges from $\mu_r + 3\sigma_r$ to $\mu_f - 3\sigma_f$.[22] The subscripts $r$ and $f$ refer to resin and fiber. On the basis of these, the interphase modulus of CF1/EP is calculated to be between 22.59 and 42.48 GPa, and that for heat treated-CF1/EP is in the range of 22.17–48.00 GPa. The upper limit of storage modulus for interphase becomes higher after 200°C/2 h heat-treatment on carbon fiber. During 200°C treatment on carbon fiber, the reactions of sizing agent may lead to a stiff layer in the

interphase region, which increases the storage modulus. In contrast, the reacted sizing component may restrict further inter-diffusion and chemical reactions with the epoxy resin during the manufacturing process of the composite. The storage moduli that belong to the interphase region are extracted and the morphologies of the interphase regions are plotted, as shown in Figure 3(d,e). After 200°C heat-treatment on carbon fiber, the interphase thickness is estimated to be 181 nm, lower than that 210 nm of CF1/EP. For CF2 composites, similar changes of interphase modulus and thickness before and after 200°C heat-treatment on carbon fiber are also obtained. The interphase modulus of CF2/EP is calculated to be between 24.47 and 57.30 GPa, and that of heat treated-CF2/EP is between 26.56 and 60.92 GPa. The interphase morphologies of CF2/EP and heat treated-CF2/EP are shown in Figure 3(f,g). After 200°C/2 h heat-treatment on carbon fiber, interphase thickness decreases from 159 to 123 nm.

Comparing the interphase modulus and thickness with IFSS results in Figure 2, the thinner interphase and higher interphase modulus after 200°C treatment on fiber correspond to higher IFSS. The relatively thin interphase of composite is better to transfer stress,[24–26] which is favorable for interfacial adhesion. However, the increased interphase modulus after 200°C/2 h heat-treatment on fiber may increase the brittleness of the region around fiber, which is adverse to energy absorption of interphase and the fracture toughness of composite,[27] proved by
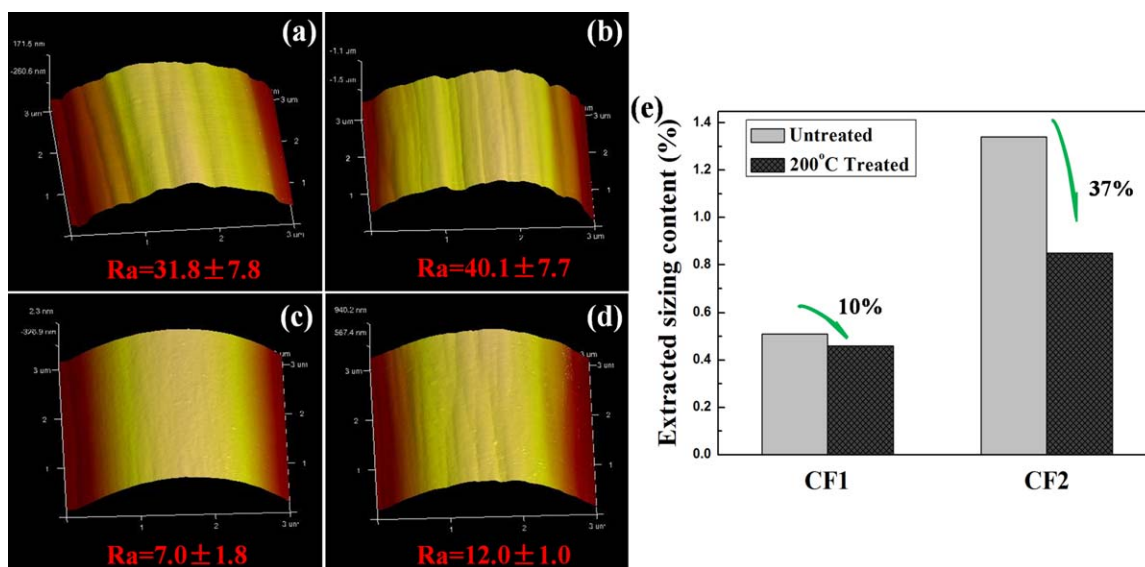
**Figure 4.** Surface morphology and roughness of (a) CF1, (b) heat treated-CF1, (c) CF2, (d) heat treated-CF2. (e) Extracted sizing content before and after 200°C/2 h heat-treatment on fiber. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Madhukar and Drzal. Tanoglu et al.[28] showed that the low strength of interphase contributed better energy absorption. These results indicate that the sizing reaction before fiber combination with resin has significant impacts on the composite interphase.

**Influence of Sizing Reaction on the Carbon Fiber Surface**

To further explore the influence reasons of sizing reaction on interphase, the effects of sizing reaction on the physicochemical properties of carbon fiber surface are firstly investigated. Surface topography was probed by AFM for the carbon fiber before and after 200°C heat-treatment, and the surface roughness was evaluated as well. From AFM images in Figure 4(a–d), it can be seen that there are regular grooves at CF1 surface and the grooves become clearer after 200°C heat-treatment. The roughness of heat treated-CF1 is 40.1 nm, higher than that 31.8 nm of CF1. For CF2, after 200°C heat-treatment, shallow and thin grooves on

CF2 surface are observed with the surface roughness increasing from 7.0 to 12.0 nm. The increased surface roughness after 200°C treatment can enhance the mechanical interlocking between fiber and matrix, favorable for improving interfacial adhesion. Figure 4(e) shows the extracted sizing contents from carbon fiber surfaces before and after 200°C treatment on fibers. After 200°C heat-treatment, the extracted sizing contents for both two fibers decrease, indicating that possible chemical reactions should have taken place between the sizing components and/or between sizing and active chemical groups at the pristine carbon fiber surface. Ten percentage drop of sizing content is observed for CF1 after 200°C heat-treatment, lower than 37% reduction for CF2.

The chemical properties of carbon fiber surface are analyzed by curve fitted of C1s spectra. Values of binding energy and the percent contribution of each curve fit to the total C1s are listed in Table II. Carbon atoms conjunct with oxygen and nitrogen

**Table II.** C(1s) Peaks of Carbon Fiber and Relative Peak Areas

| Carbon fiber | C1(s) peaks in different states BE (eV; area %) | | | | | | Activated carbon (%) |
|---|---|---|---|---|---|---|---|
| | Peak 1 284.8 eV | Peak 2 286.1 eV | Peak 3 286.6 eV | Peak 4 287.7 eV | Peak 5 289.4 eV | Peak 6 290.6 eV | |
| CF1 | 69.71 | 14.40 | 15.73 | 0 | 0.16 | 0 | 30.29 |
| Desized-CF1 | 64.76 | 13.53 | 20.95 | 0 | 0.76 | 0 | 35.24 |
| Heat treated-CF1 | 85.63 | 1.08 | 12.62 | 0 | 0.67 | 0 | 14.37 |
| Desized-heat treated-CF1 | 80.81 | 17.49 | 0.55 | 1.16 | 0 | 0 | 19.19 |
| CF2 | 59.70 | 31.87 | 1.94 | 1.14 | 5.36 | 0 | 40.30 |
| Desized-CF2 | 70.47 | 5.33 | 23.17 | 0 | 1.04 | 0 | 29.53 |
| Heat treated-CF2 | 36.92 | 0 | 48.67 | 14.41 | 0 | 0 | 63.08 |
| Desized-heat treated-CF2 | 73.38 | 0 | 19.73 | 6.89 | 0 | 0 | 26.62 |
| Peak assignment | Reference —C—C— —C—H— | —C—OH —C—O— —C—NH$_2$ | C—O—C=O Epoxide | —C=O —C=N | —O—C=O HO—C=O | —COO$^-$ $\pi$–$\pi^*$ | |

are defined as activated carbon atoms, which can be achieved from the sum of Peak 2 to Peak 6. Compared CF1 with heat treated-CF1, the activated carbon content decreases from 30.29 to 14.37% after 200°C treatment, along with concentration reductions of —C—OH, —C—O—, and —C—NH$_2$ groups (Peak 2) and C—O—C═O and epoxide groups (Peak 3). In combination with the FTIR results in Figure 1(a), this should be ascribed to the reactions of active hydrogen from amine and hydroxyl in sizing with epoxide group. Significant content decline of Peak 3 from 20.95% to 0.55% can be seen, by comparing desized-heat treated-CF1 with desized-CF1. Meanwhile, the desized-heat treated-CF1 shows 17.49% concentration of Peak 2, slightly higher than 13.53% that of desized-CF1. The results suggest that sizing agent can fully react with the functional groups on the pristine carbon fiber surface. The reaction products between sizing and fiber are difficult to dissolve into acetone, which is consistent with the lower reduction in sizing extraction content for CF1 in Figure 4(e). For CF2, similarly, the chemical properties on CF2 and heat treated-CF2 surfaces are firstly compared. Percentage of activated carbon atoms on heat treated-CF2 surface is 63.08%, higher than that of 40.3% on CF2 surface. There are 31.87% concentration of Peak 2 and 5.36% concentration of —O—C═O and HO—C═O groups (Peak 5) on CF2; however, these two peaks disappear along with the dramatic content increase of functional groups in Peak
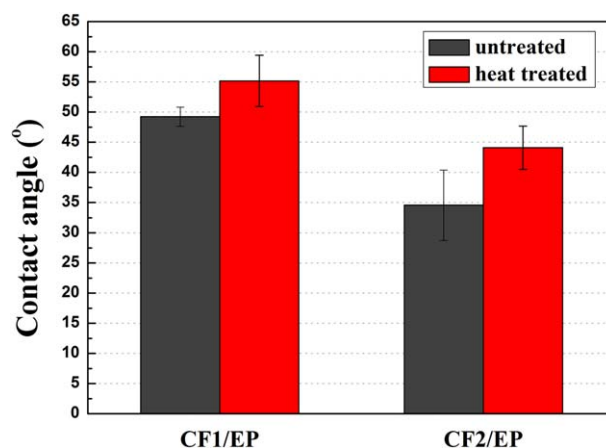


**Figure 5.** Contact angle at 80°C of carbon fiber before and after 200°C treatment with EP resin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

3 and Peak 4 after 200°C heat-treatment. Combined with the FTIR results in Figure 2(a), this indicates that the chemical reactions mainly occur between hydroxyl and carboxyl groups during 200°C/2 h heat-treatment. Compared desized-CF2 with desized-heat treated-CF2, percentage of activated carbon atoms on desized-heat treated-CF2 decreases, and the group contents
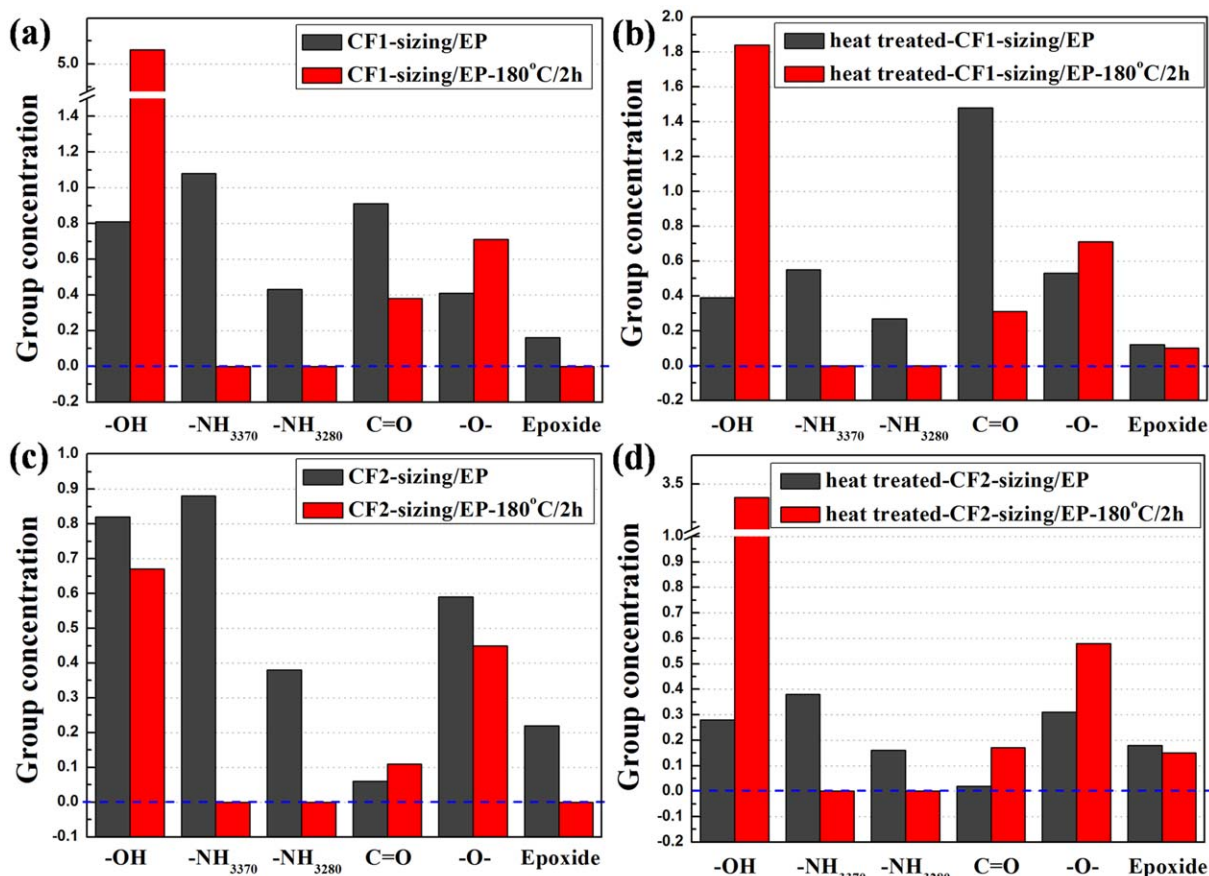


**Figure 6.** Concentration change of typical functional groups of sizing/EP mixture after 180°C/2 h treatment: (a) CF1-sizing/EP, (b) heat treated-CF1-sizing/EP, (c) CF2-sizing/EP, and (d) heat treated-CF2-sizing/EP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
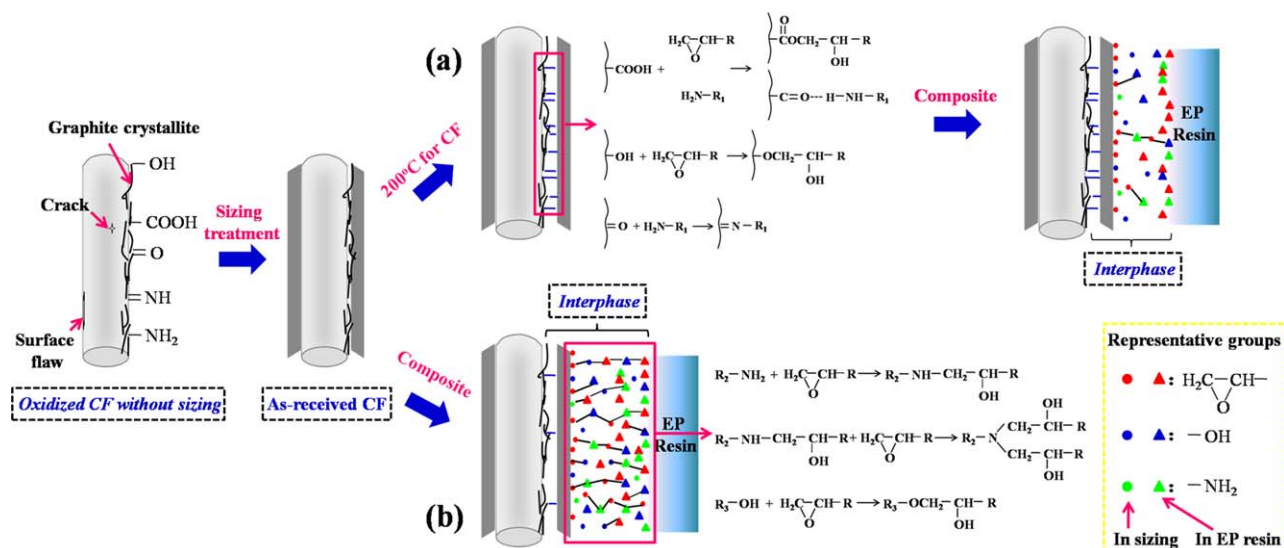
**Figure 7.** Schematic showing effect mechanism of sizing reaction on composite interphase region: (a) carbon fiber after 200°C treatment and then composited with EP matrix, (b) carbon fiber directly composited with EP matrix. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of Peak 2, Peak 3, and Peak 5 as well, also suggesting that fully reactions occurred between fiber and sizing. However, unlike CF1, the reaction products on CF2 during 200°C treatment can dissolve in acetone and can be extracted from fiber surface. Thus, greater reduction in sizing extraction content for CF2 is observed in Figure 4(e). Therefore, the 200°C treatment on carbon fiber promotes the chemical reactions of sizing itself and sizing with active groups on the pristine carbon fiber surface. This will result in a stiff layer in the vicinity of the carbon fiber and increase the interphase modulus.

Analyses above have shown that surface roughness and chemical properties are changed after sizing reaction, which will certainly affect the wettability of fiber with matrix. Herein, contact angle between fiber and matrix was measured to evaluate their wettability, as shown in Figure 5. After 200°C treatment on fibers, the contact angles of carbon fibers with EP matrix increase for both CF1 and CF2, indicating lower wettability after the sizing reaction, which is unfavorable for sufficient molecular diffusions and subsequent chemical reactions between the sizing and the EP resin.

### Chemical Reactions Between Sizing Agent and Epoxy

Chemical reactions between sizing agent and EP resin were analyzed by FTIR. The mixtures of CF-sizing/EP and heat treated-CF-sizing/EP were both treated at 180°C for 2 h. The concentration changes of the functional groups are shown in Figure 6. Figure 6(a) shows that after 180°C treatment, hydroxyl group increases, N—H and epoxide groups vanish for the mixture of CF1-sizing/EP. For the mixture of heat treated-CF1-sizing/EP [Figure 6(b)], the increased hydroxyl group and disappeared N—H group are also observed, while there is only slight decrease of epoxide group. Similar tendency is also revealed for the mixtures of CF2-sizing/EP and heat treated-CF2-sizing/EP, as shown in Figure 6(c,d). Since CF1-sizing and CF2-sizing both contain epoxide group, similar with the EP resin, the

variation of epoxide group can reflect the degree of chemical reactions between sizing agent and EP matrix. The results demonstrate that the 200°C/2 h treatment on carbon fiber, that is, sizing reacted before fiber composited with matrix, greatly restrained the physical interdiffusion and chemical reactions between sizing agent and EP matrix at interphase.

To clearly understand the effects of sizing reaction, a schematic showing the mechanism is illustrated in Figure 7. As shown in Scheme (a), the sizing agent can fully react itself and with the active groups on the pristine carbon fiber during 200°C heat-treatment on fiber, which will result in a stiff layer on the carbon fiber surface and increase the interphase modulus. At the same time, this will inhibit the diffusion of sizing components into the EP resin and reduce potential chemical reactions between them. A thin interphase region is obtained, which is better for stress transfer. It is worth noting that, in general, sizing agent contains no or less cure agent than stoichiometric amount. Therefore, the uncured components may diffuse and react with the EP resin, enhancing the interfacial adhesion. When the sized fiber directly composites with EP resin [Scheme (b)], the molecule diffusion and reactions may be sufficient between sizing and EP resin. Correspondingly, the interphase region becomes thicker. The possible chemical reactions of sizing with functional groups on fiber surface and EP resin are respectively shown in Scheme (a) and (b).

### CONCLUSIONS

Temperature resistance of the sizing agent is important to the structure and performance of the interphase region for carbon fiber composites. On the basis of this, effects of sizing reaction on the interphase of carbon fiber/epoxy composite were investigated through 200°C/2 h treatment on two types of carbon fiber. The IFSSs of the carbon fiber/epoxy showed improvement of 10–11% after the 200°C heat-treatment. Dynamic mechanical mapping analysis revealed that the interphase region was

averagely thinner with higher storage modulus for the 200°C treated carbon fiber composite. Further analyses indicated that during 200°C treatment, the sizing agent can react itself and with active groups on pristine surface of the carbon fiber as well, which could explain the formation of stiffer layer in vicinity of the carbon fiber. Moreover, changes of the interphase region should be also associated with the increased fiber surface roughness, the lowered resin wettability, and the reduced chemical reactions between sizing and resin, due to the heat-treatment on the carbon fiber.

## REFERENCES

1. Soutis, C. *Prog. Aerosp. Sci.* **2005**, *41*, 143.

2. Cho, D.; Drzal, L. T. *J. Appl. Polym. Sci.* **2000**, *75*, 1278.

3. Mimura, K.; Ito, H.; Fujioka, H. *Polymer* **2000**, *41*, 4451.

4. Odagiri, N.; Kishi, H.; Yamashita, M. *Adv. Compos. Mater.* **1996**, *5*, 249.

5. Kim, K. Y.; Ye, L. *Compos. Part. A: Appl. Sci.* **2004**, *35*, 477.

6. Pegoretti, A.; Fambri, L.; Migliaresi, C. *Polym. Compos.* **2000**, *21*, 466.

7. Plonka, R.; Mäder, E.; Gao, S. L.; Bellmann, C.; Dutschk, V.; Zhandarov, S. *Compos. Part. A: Appl. Sci.* **2004**, *35*, 1207.

8. Sharma, M.; Gao, S. L.; Mäder, E.; Sharma, H.; Wei, L. Y.; Bijwe, J. *Compos. Sci. Technol.* **2014**, *102*, 35.

9. Jones, F. R. *J. Adhes. Sci. Technol.* **2010**, *24*, 171.

10. Weitzsacker, C. L.; Xie, M.; Drzal, L. T. *Surf. Interface Anal.* **1997**, *25*, 53.

11. Liu, H. X.; Gu, Y. Z.; Li, M.; Zhang, D. M.; Li, Y. X.; Zhang, Z. G. *Polym. Compos.* **2012**, *33*, 1368.

12. Cho, D.; Choi, Y.; Drzal, L. T. *J. Adhes.* **2003**, *79*, 1.

13. Cho, D.; Choi, Y.; Chang, J. H.; Drzal, L. T. *Compos. Interface* **2006**, *13*, 215.

14. Miyazaki, M.; Wakoh, Y.; Inoue, H. U.S. Patent 5,093,155 (**1992**).

15. Liu, W. B.; Zhang, S.; Hao, L. F.; Jiao, W. C.; Yang, F.; Li, X. F.; Wang, R. G. *J. Appl. Polym. Sci.* **2013**, *128*, 3702.

16. Cao, X.; Wen, Y. F.; Zhang, S. C.; Yang, Y. G. *New Carbon Mater.* **2006**, *21*, 337.

17. Dai, Z. S.; Zhang, B. Y.; Shi, F. H.; Li, M.; Zhang, Z. G.; Gu, Y. Z. *J. Appl. Polym. Sci.* **2012**, *124*, 2127.

18. Yao, L. R.; Li, M.; Wu, Q.; Dai, Z. S.; Gu, Y. Z.; Li, Y. X.; Zhang, Z. G. *Appl. Suf. Sci.* **2012**, *263*, 326.

19. Wu, Q.; Li, M.; Gu, Y. Z.; Wang, S. K.; Yao, L. R.; Zhang, Z. G. *Polym. Compos.* **2014**, DOI:10.1002/pc.23176.

20. Gao, S. L.; Mader, E. *Compos. Part. A: Appl. Sci.* **2002**, *33*, 559.

21. Kim, J. K.; Hodzic, A. *J. Adhes.* **2003**, *79*, 383.

22. Gu, Y. Z.; Li, M.; Wang, J.; Zhang, Z. G. *Carbon* **2010**, *48*, 3229.

23. Cho, D.; Choi, Y.; Chang, J. H.; Drzal, L. T. *Polymer* **2001**, *42*, 4611.

24. Upadhyaya, D.; Tsakiropoulos, P. *J. Mater. Process. Technol.* **1995**, *54*, 17.

25. Chang, J.; Bell, J. P.; Joseph, R. *SAMPE Q.* **1987**, *18*, 39.

26. Hughes, J. D. H. *Compos. Sci. Technol.* **1991**, *41*, 13.

27. Madhukar, M. S.; Drzal, L. T. *J. Compos. Mater.* **1992**, *26*, 936.

28. Tanoglu, M.; McKnight, S. H.; Palmese, G. R.; Gillespie, J. W., Jr. *Compos. Sci. Technol.* **2001**, *61*, 205.