Research Article

Effect of Sizing Agents on Surface Properties of T800 Grade CF and Thermal Aging Time on Mechanical Properties of T800 Grade CF/Epoxy Composites

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This paper investigates the effect of sizing agent molecular weight on carbon fiber (CF) surface properties and the effect of thermal aging time on mechanical properties of CF/epoxy composites. The surface properties of three CCF800 CF samples with varying sizing agent molecular weight were characterized by surface morphology, surface roughness, chemical functional groups, and element composition. The results showed that the sample with low molecular weight exhibited low roughness and high proportion of activated carbon atoms. The flexural strength, flexural modulus, and interlaminar shear strength of CCF800/5228 composites were measured at 25°C and 150°C by thermal ageing time 0, 100 h, 250 h, 500 h, and 1000 h. The results showed that the thermal aging time up to 1000 h had little effect on the flexural modulus, and the interlaminar shear performance at 150°C showed a trend of increasing at the beginning and then decreasing.

1. Introduction

As indispensable reinforcing materials used in advanced composites, carbon fibers (CF) have a series of excellent properties, including high specific strength and modulus, excellent thermal, fatigue, and chemical corrosion resistance [1–3]. CF reinforced composites are suitable for applications such as satellites, launch vehicles, or aircrafts, for reducing weight or improving mechanical performance [4–6]. During their production process, CF must be sized after oxidation treatment, coating a layer of tens to hundreds of nanometers thick organic sizing agents on the surface [7]. Except processability improvement, sizing agents can also effectively increase surface energy and produce active functional groups, which improve wettability and interface bonding performance between CF and matrix [8, 9]. In addition, sizing agents can change surface appearance by generating uneven folds and increasing roughness, which are benefit to interface bonding strength by "anchor

effect" [10–12]. In order to acquire one optimized sizing agent for a specific CF reinforced composite, researchers have made many attempts for analyzing different factors of sizing agents, such as chemical composition, molecular weight, dispersion of function groups, solution properties, or molecular modification [13–19]. Among them, molecular weight is considered as an important factor influencing on surface roughness and thermal stability. When applying CF reinforced epoxy matrix composites, actual service life was affected by environment elements, such as temperature, humidity, and ultraviolet light [20]. Thermal aging was pointed out as a main form of composite corrosion failure, which decreased mechanical properties in long time service [21].

As Chinese T800 grade CF are in rapid development, the effect of sizing agents on CCF800 (one of Chinese T800 grade CF) surface properties and the thermal aging properties of CCF800 reinforced composites are worth to be investigated. Three sizing agents varying in molecular

weight were coated on CCF800 CF during manufacture process. The surface morphology, surface roughness, chemical functional groups, and element composition were measured, and the results were compared and analyzed to describe the effect of sizing agents. The unidirectional and 60% fiber volume fraction CCF800/5228 composites were made from prepregs. The thermal ageing time was set from 0 to 1000 h. The flexural strength, flexural modulus, and interlaminar shear strength were measured at 25°C and 150°C in 0, 100 h, 250 h, 500 h, and 1000 h by ASTM standards. The results exhibited the trends of different mechanical properties during thermal aging.

2. Experiment

2.1. Materials. The nominal molecular weight of three sizing agents is shown in Table 1. These sizing agents were sized on CCF800 during manufacture process. Epoxy resin 5228 was obtained from Beijing Institute of Aeronautical Materials. The solvent ethyl alcohol was purchased from Beijing Chemical Works. All reagents were of analytical grade. CCF800/5228 composites were made by prepreg autoclave forming process at 180°C for 3 h. CCF800 were unidirectional arranged, and the volume fraction of fiber was 60%.

2.2. Characterization of CCF800. The linear density was tested in accordance with the standard GB/T 3362-2017 Appendix B and the bulk density in accordance with the standard GB/T 30019-2013 method A.

The surface morphology was acquired using JSM-7500 cold field emission scanning electron microscope (SEM) and Veeco D3000 atomic force microscope (AFM). The scanning area of AFM was selected as $3 \mu m \times 3 \mu m$. The software Nano Scope was used to calculate average surface roughness.

The surface chemical functional groups and element composition were analyzed using Thermo Nicolet Nexus 470 Fourier transform infrared spectrometer (FTIR) and ESCA-LAB250 X-ray photoelectron spectrometer (XPS). The infrared spectrum spectra were obtained from $3500 \mathrm{cm}^{-1}$ to $500 \mathrm{cm}^{-1}$. The XPS measurements were carried out by both full-spectrum scanning and high-precision narrow-spectrum scanning. C1s peak was selected to determine the form and proportion of carbon using the XPS Peak software.

2.3. Thermal Stability of Sizing Agents. The sizing agent samples were extracted from CCF800. The thermal stability was performed using the STA449 F3 TG-DSC synchronous thermal analyzer produced by the German NETZSCH company. The weight loss was recorded from room temperature to 500°C with a 10°C/min heating rate. Two types of thermogravimetric measurement atmosphere, the nitrogen and air, were selected in this experiment.

2.4. Thermal Aging Properties of CCF800/5228 Composites. The heat treatment condition was set to (150 ± 5)°C with six groups of ageing time 0, 100, 250, 500, 750, and 1000 h. For each group, flexural strength, flexural modulus, and interlaminar shear strength were tested in both (25 ± 3)°C and (150 ± 5)°C. Experimental samples, testing machines,

TABLE 1: The nominal sizing agent molecular weight.

CF	Molecular weight of sizing agent
CCF800A	1520
CCF800B	4690
CCF800C	21400

TABLE 2: The linear and bulk density tests of carbon fiber.

Carbon fiber	Linear density (g/km)	Bulk density (g/cm^3)
CCF800A	449 ± 1	1.782 ± 0.005
CCF800B	443 ± 2	1.788 ± 0.003
CCF800C	448 ± 1	1.784 ± 0.005

and procedures were in accordance with the standard ASTM D7264 for flexural strength and flexural modulus and the standard ASTM D2344 for interlaminar shear strength.

3. Results and Discussions

3.1. Linear and Bulk Density. From the results in Table 2, the difference of maximum and minimum bulk density among three CF was 0.006 g/cm^3 (0.33%), indicating no significant variation. Bulk density is an inherent property of CF and often reflects graphite compactness, which is determined by production process. Three CCF800 samples were manufactured in the same process, and this was consistent with the experimental values. Similar situation was also found in the linear density measurements. Linear density of CF is only affected by fiber diameter and bulk density. Thus, it was concluded that molecular weight of sizing agents did not influence bulk density, linear density, and diameters of CF.

3.2. Surface Morphology and Roughness. The surface and fracture section morphology were observed by SEM as shown in Figure 1. Obvious "grooves" on the surface were found, distributing along the fiber direction. Among three samples, the length, number, and distribution of grooves were almost in the same level, which meant the effect of molecular weight on these factors could not be found by SEM measurement. As a brittle material, the fracture of CF normally generates from crack propagation. Figure 1 exhibits such fracture mode and records the crack sources with different locations. Seen from photos (b) and (d) in Figure 1, the fracture direction was easily found from one specific crack source starting from the surface, while photo (f) exhibited three crack sources of fracture. Therefore, molecular weight of sizing agents might influence the number and location of crack sources.

From AFM three-dimensional images in Figure 2, several grooves were seen clearly along the fiber axis on the surface. In the selected $3 \mu m \times 3 \mu m$ area, the height of
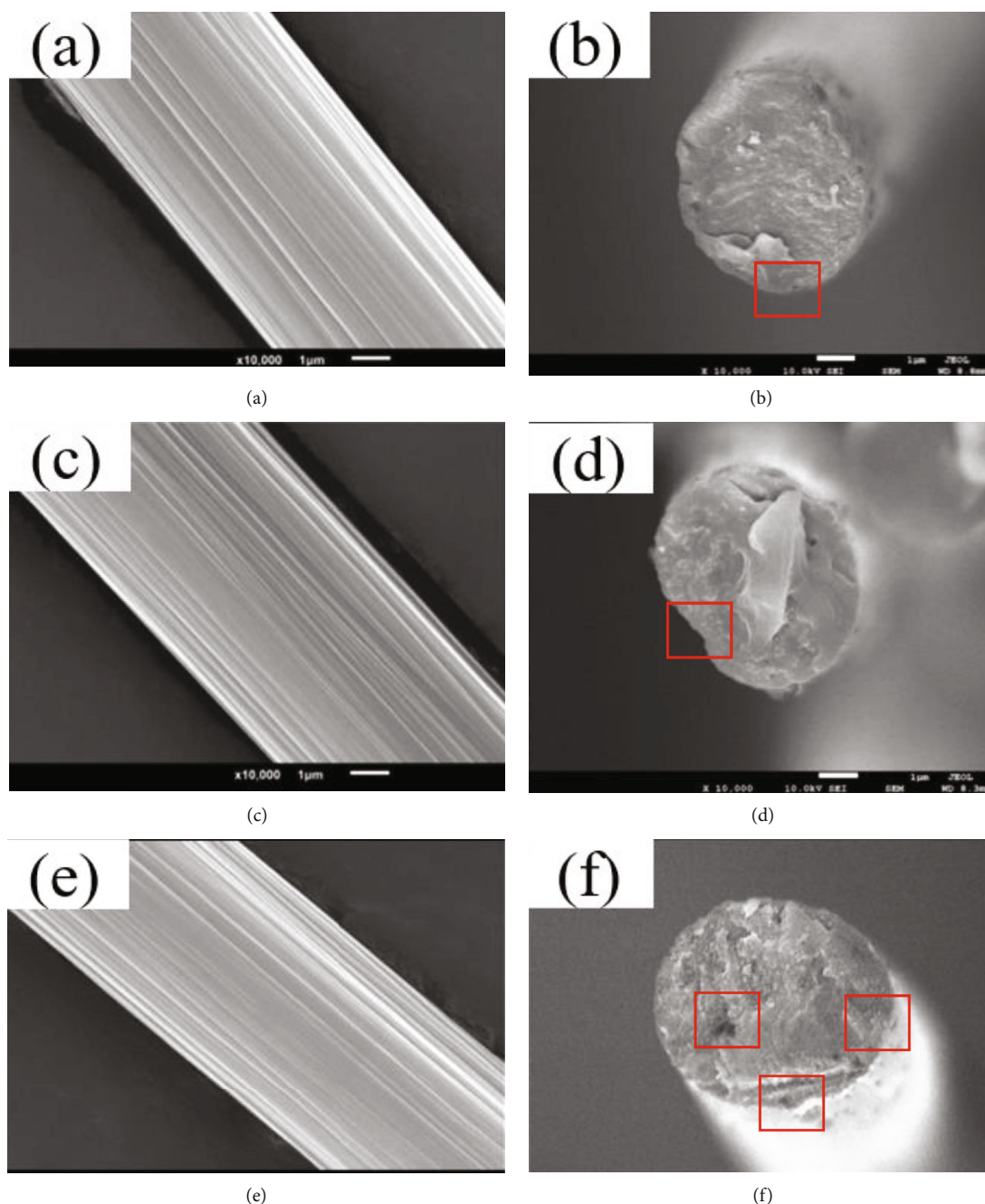
Figure 1: The morphology of surface and fracture section: (a, b) CCF800A; (c, d) CCF800B; (e, f) CCF800C.

CCF800A surface was the smallest among these three CF, which reflected the lowest surface roughness in Table 3. The surface roughness of CCF800B and CCF800C were quite similar, 32.63 nm and 32.60 nm, respectively, and that of CCF800A was 25% less. It proved that molecular weight of sizing agents had an effect on surface roughness, and CF with small molecular weight of sizing agents exhibited low surface roughness.

3.3. Surface Chemical Functional Groups and Element Composition. Seven signification peaks appeared in Figure 3,

$2960 \, cm^{-1}$ (asymmetric stretching vibration -CH_3), $1727 \, cm^{-1}$ (-CHO flexural vibration peak), $1506 \, cm^{-1}$ (benzene ring vibration peak), $1250 \, cm^{-1}$ (typical epoxide C-O peak), $1044 \, cm^{-1}$ (-CO- flexural vibration peak), $916 \, cm^{-1}$ (terminal epoxy ring peak), and $830 \, cm^{-1}$ (para-substituted benzene ring out-of-plane deformation and cis-epoxide C-O peak). According to the typical epoxide C-O, cis-epoxide C-O, or terminal epoxy ring peak, it was speculated that bisphenol A epoxy resin was main component of these sizing agents. Thus, these sizing agents were suitable for epoxy resin in manufacturing composites.
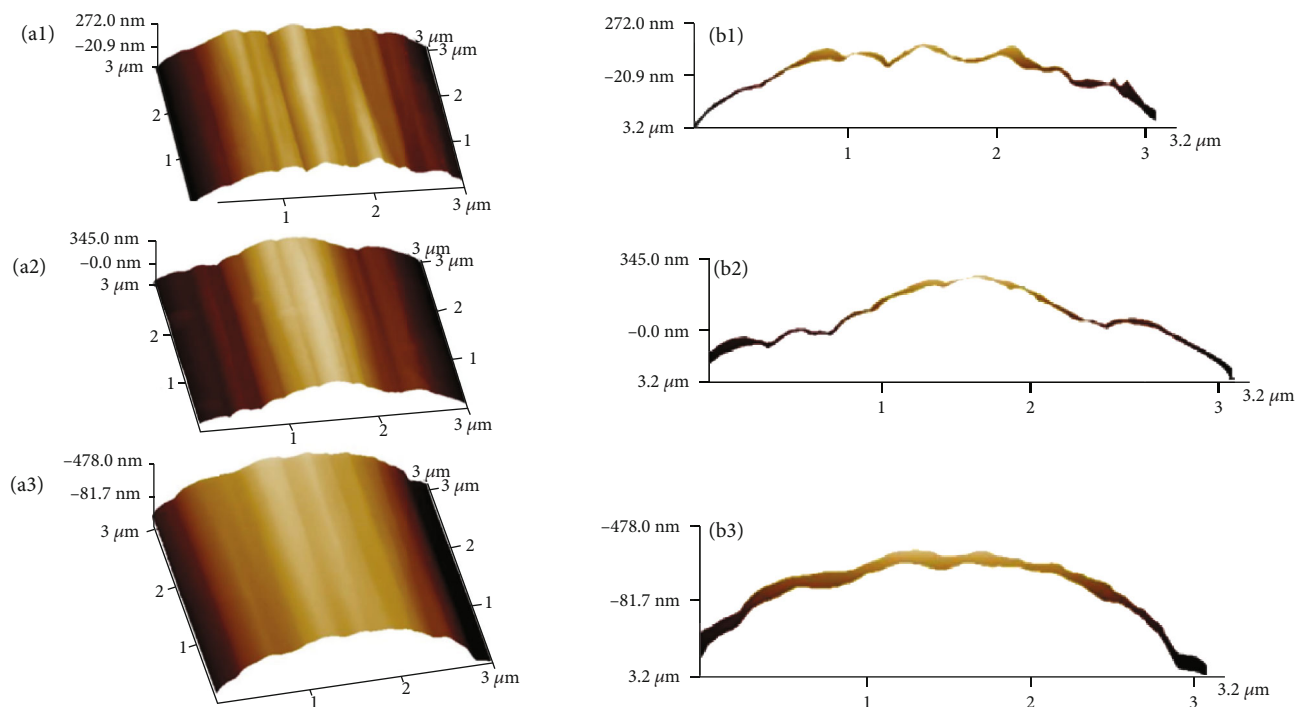
FIGURE 2: The surface AFM topography of carbon fibers: (a) CCF800A; (b) CCF800B; (c) CCF800C.

TABLE 3: The surface roughness of carbon fiber.

Carbon fiber	Roughness (Ra/nm)
CCF800A	24.58 ± 1.01
CCF800B	32.63 ± 3.56
CCF800C	32.60 ± 2.32

As detection depth of full-spectrum scanning XPS was no more than 10 nm and thickness of sizing agents coated on the surface was normally tens to hundreds of nanometers [7], XPS analysis of CF was regarded as elemental analysis of sizing agents. From the results in Figure 4, there were two strong peaks, 287 eV for C1s peak and 531 eV for O1s peak. With outstanding elements C and O, the conjecture that sizing agents used bisphenol A epoxy resin as the main component was further proved.

In order to find out the form and proportion of element C, the narrow XPS scanning of the C1s fitting peak was obtained by the XPS Peak software as shown in Figure 5. The fitting results are listed in Table 4. The meaningful point was that the activated carbon atom ratio of CCF800A (32.66%) was much higher that CCF800B (27.34%) and CCF800C (28.54%). Thus, CF with low molecular weight of sizing agents exhibited high activated carbon atom proportion.

3.4. Thermal Stability of Sizing Agents. TG curves are shown in Figure 6, and the temperatures of 5% and 10% weight loss
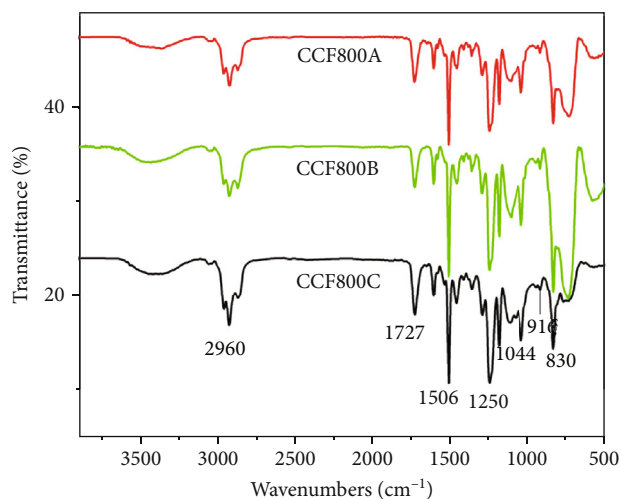

FIGURE 3: The Fourier transform infrared spectra of CF.

for each sample are listed in Table 5. It was seen that the temperatures of 5% weight loss of these three agents were above 270°C in both N_2 and air. Both the temperatures of 5% or 10% of CCF800C were a little higher than those of CCF800A and CCF800B, which meant high molecular weight improved the thermal stability, but the improvement was limited and not meaningful.

When temperature reached over 300°C, the lost in weight became more severe. As thermal decomposition temperature of epoxy resin is normally 300°C, these curves in
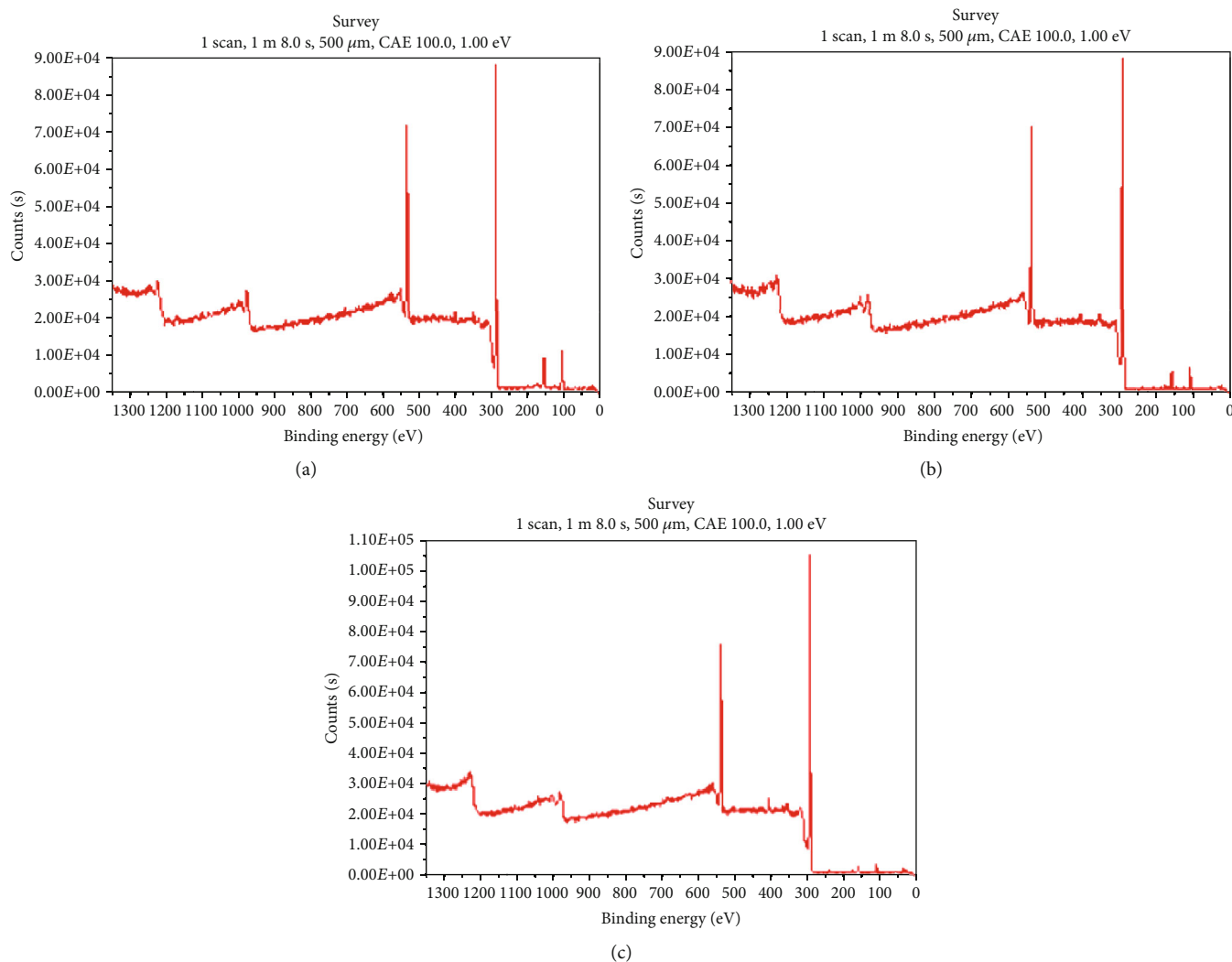
(a)

(b)

(c)

FIGURE 4: The XPS full-spectrum scanning results: (a) CCF800A; (b) CCF800B; (c) CCF800C.

Figure 6 further proved that the sizing agents were speculated to use bisphenol A epoxy resin as main component.

3.5. Thermal Aging Properties of CCF800/5228 Composites. During long-term thermal aging, plasticization degree of thermosetting resin matrix composites reduces, while rigidity and brittleness increase. In a particular aging term, thermal treatment at a temperature below matrix glass transition temperature causes shrinkage of free volume, which leads to increase of density, rigidity, and tensile strength and decrease of toughness. In addition, expansion mismatch problem between matrix and CF often causes damage to interface, leading to mechanical property reduction. As thermal treatment at an appropriate temperature can also bring about postcuring reaction for thermosetting resin matrix composites, the relationship between thermal aging time and mechanical properties in service life of composites is complicated.

The thermal aging properties of CCF800/5228 composites are listed in Tables 6 and 7. First, the flexural strength and interlaminar shear strength at 150°C testing temperature significantly reduced (about 20% and 30%), comparing those at 25°C. The mechanical properties of 5228 matrix decreased at 150°C, and unevenness thermal expansion of CCF800 and 5228 matrix were considered as main reasons. Second, thermal aging time up to 1000 h had little effect on the flexural modulus of CCF800/5228 composites at 150°C. With the increasing aging time, the modulus fluctuated within a small range (114 to 118 GPa), as well as the standard deviation (2 to 5 GPa). It could be explained that 150°C/1000 h treatment brought no changes to CF, and the flexural modulus was mainly determined by CF. Third, with the extension of aging time, the flexural strength showed a trend of rising from 1516 ± 62 to 1612 ± 56 MPa, indicating that postcuring reaction occurred. Fourth, as the aging time prolonged, the interlaminar shear performance at 25°C slightly reduced and that at 150°C showed a trend of first increasing and then decreasing. After 500 h, the interlaminar shear strength increased from 75 ± 1 to 80 ± 2 MPa. The postcuring reaction and internal stress release could be the reasons for that trend.
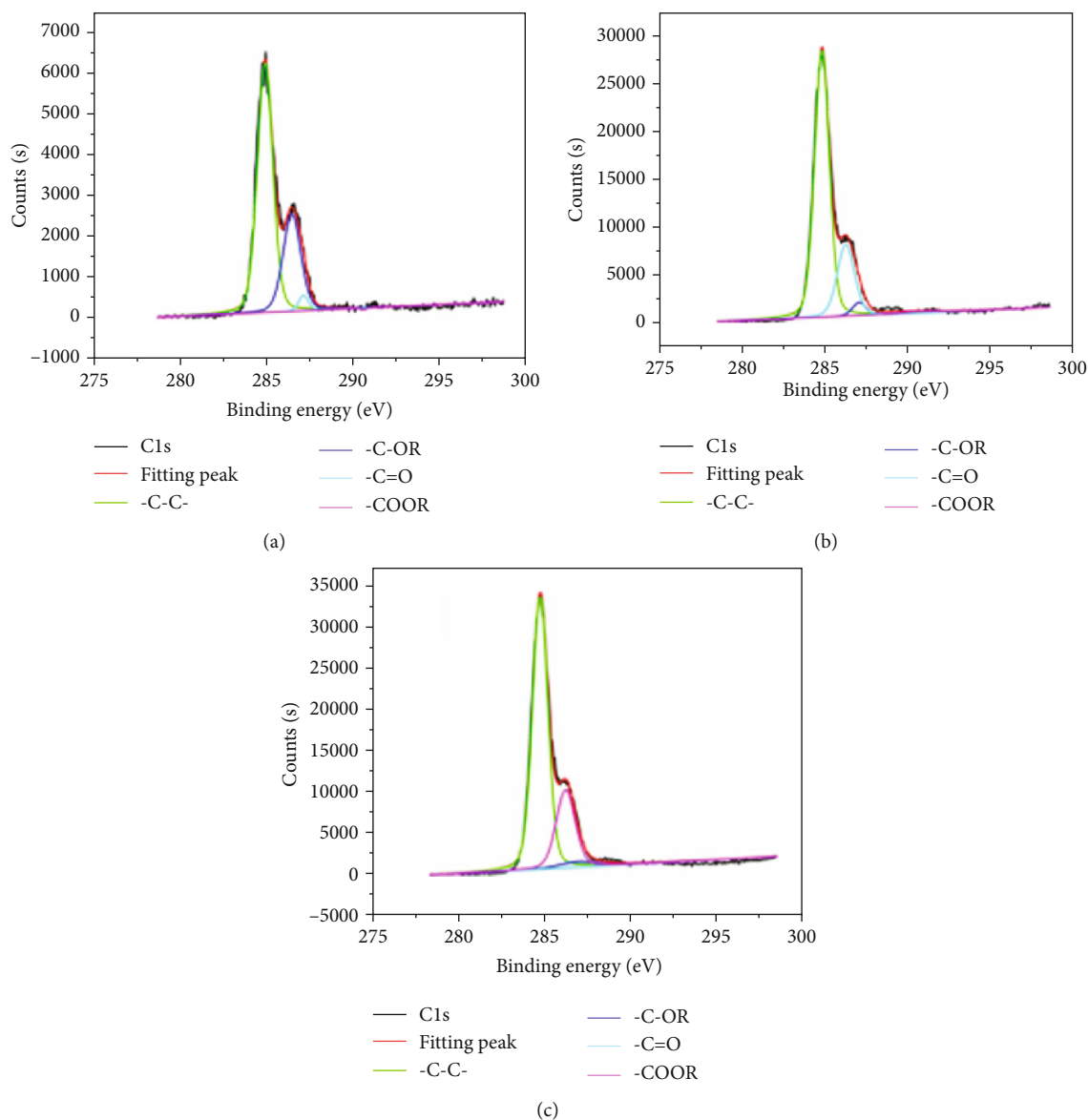
(a)

(b)

(c)

FIGURE 5: The XPS narrow scanning results of C1s fitting peak: (a) CCF800A; (b) CCF800B; (c) CCF800C.

TABLE 4: The fitting results of C1s peak.

Carbon fiber	-C-C- or –C-H 284.8 eV	-C-OH or –C-OR 286.3 eV	-C=O 287.0 eV	-COOH or -COOR 290.0 eV	Activated carbon atom ratio/%
CCF800A	67.34	30.00	2.62	0.11	32.66
CCF800B	72.66	22.93	3.22	1.19	27.34
CCF800C	71.46	25.25	3.02	0.38	28.54

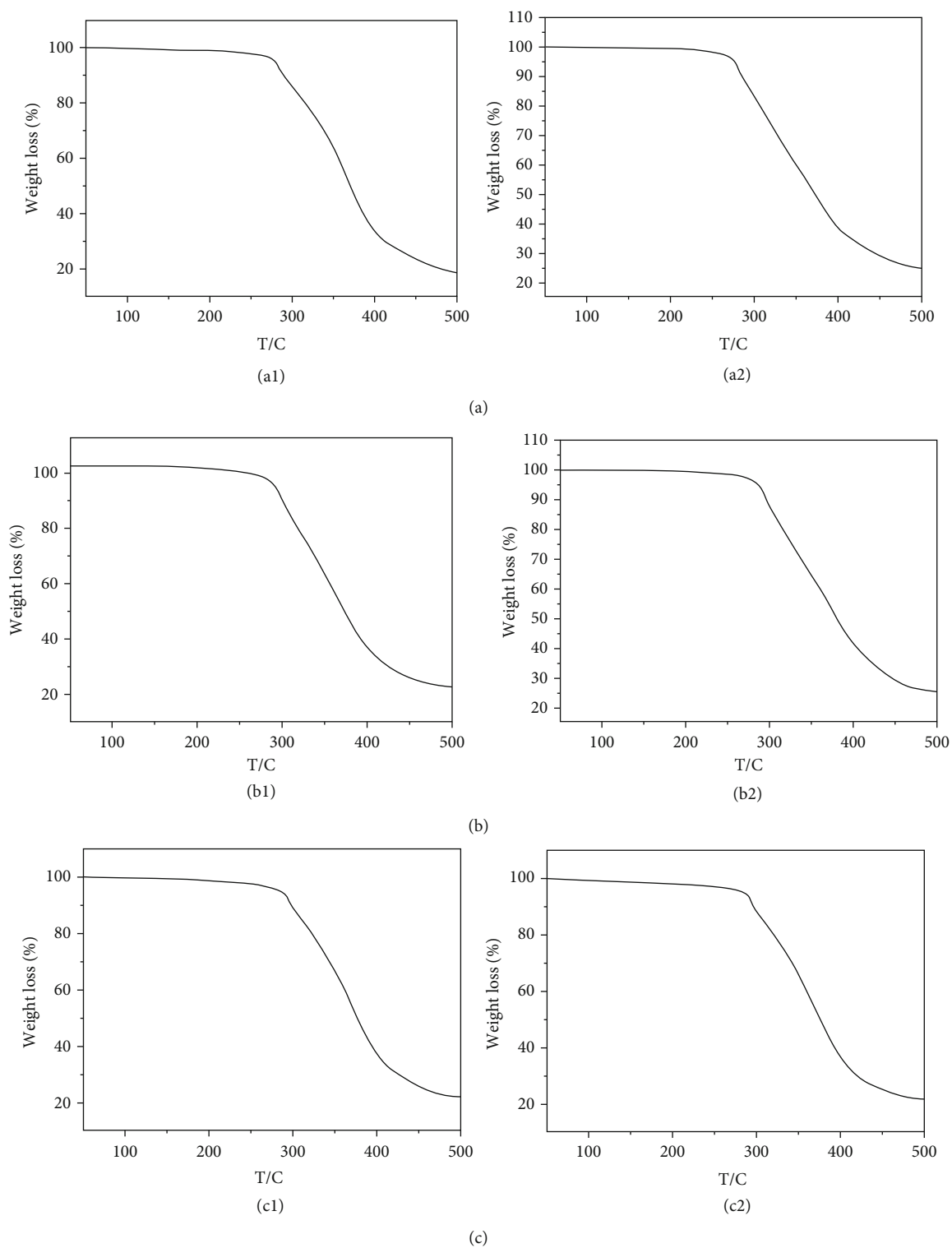(a1)

(a2)

(a)

(b1)

(b2)

(b)

(c1)

(c2)

(c)

FIGURE 6: TG curves in N_2 and air atmosphere (1, N_2; 2, air): (a) CCF800A; (b) CCF800B; (c) CCF800C.

TABLE 5: The weight loss of sizing agents.

Carbon fiber	Temperature of 5% weight loss (°C)		Temperature of 10% weight loss (°C)	
	N$_2$	Air	N$_2$	Air
CCF800A	279.3	275.9	289.4	285.6
CCF800B	283.8	286.2	295.8	294.9
CCF800C	285.9	282.8	297.7	297.2

TABLE 6: The thermal aging properties of CCF800/5228 composites—flexural strength and modulus.

	Flexural strength (MPa)					Flexural modulus (GPa)				
Test temperature	Room temperature (25°C)		150°C		Retention rate (%)	Room temperature (25°C)		150°C		Retention rate (%)
Aging time (h)	Average value	Standard deviation	Average value	Standard deviation		Average value	Standard deviation	Average value	Standard deviation	
0	1516	61	1220	44	80	117	5	118	4	101
100	1566	78	1187	24	76	116	4	114	4	98
250	1589	40	1215	27	76	115	4	116	2	101
500	1609	57	1259	72	78	116	4	115	4	99
750	1603	75	1288	36	80	117	3	116	4	99
1000	1612	56	1235	60	77	117	4	116	4	99

TABLE 7: The thermal aging properties of CCF800/5228 composites—interlaminar shear strength.

	Interlaminar shear strength (MPa)				
Test temperature	Room temperature (25°C)		150°C		Retention rate (%)
Aging time (h)	Average value	Standard deviation	Average value	Standard deviation	
0	107	2	75	1	70
100	107	5	78	2	73
250	106	4	79	3	75
500	103	3	80	2	78
750	105	3	75	2	71
1000	105	2	77	2	73

Fifth, synthesizing the interlaminar shear strength results from 0 h to 1000 h; the retention rate of 150°C was higher than 70%.

4. Conclusions

CCF800 CF coated with three sizing agents varying in molecular weight were studied. The change of molecular weight did not influence the length, number, and distribution of surface grooves much. CCF800 CF with small molecular weight of sizing agent exhibited low surface roughness and high activated carbon atom proportion. After thermal aging at 150°C, the flexural strength and interlaminar shear strength of CCF800/5228 composites reduced significantly, comparing those at 25°C, while thermal aging had little effect on the flexural modulus. For CCF800/5228 composites, the retention rate of interlaminar shear strength at 150°C was higher than 70% from 0 to 1000 h. The interlaminar shear performance at 150°C showed a trend of increasing at the beginning and then decreasing.

Data Availability

Some or all data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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