Effect of Two-Step Surface Treatment on the Mechanical Properties of Hollow Integrated Core Sandwich Composites with GF/CF Hybrid Face Sheets

Kejing Yu, Haijian Cao, Kun Qian, Hongshun Li, Juanjuan Wang

Key Laboratory of Eco-textiles, Ministry of Education, Wuxi, Jiangsu CHINA

Correspondence to:
Haijian Cao email: caohaijian20010@163.com

ABSTRACT

In this study, the effect of a two-step surface treatment on the mechanical properties of hollow integrated core sandwich composites with glass fiber/carbon fiber (GF/CF) hybrid face sheets were investigated. The presence of functional groups on the surface during the two-step treatment was characterized by Fourier transform infrared spectrometer (FTIR). The results of tensile strength on single filaments indicated that no extra loss of fiber strength was observed after the two-step surface treatment for both the glass and carbon fibers. Scanning electron microscopy (SEM) data confirmed the positive effect of the two-step surface treatment on the hollow integrated core sandwich fabric with GF/CF hybrid face sheets. It was found that the hollow integrated core sandwich composites with GF/CF hybrid face sheets showed significant improvements in tensile strength, bending strength and compression strength after the two-step surface treatment, which indicated the two-step surface treatment was efficient.

Keywords: textile composites; glass fibers; Carbon fibers; mechanical properties; surface treatments

INTRODUCTION

In recent years, hollow integrated core sandwich fabric reinforced composites have attracted lots of attention, owing to their promising potential applications in many different fields, such as the aerospace, marine, locomotive and automobile industries [1,2]. It is known that the fiber performance in integrated core sandwiches is three-dimensional and consists of two bi-directional woven fabric surfaces, which are mechanically connected with vertical woven ply. However, the high weave density of the fabrics often affects the impregnation of the fibers by the resin when the matrix resin is injected into the fabric. The generation of voids and defects at the interface affects the load transfer between the fibers and the matrix, which affects the overall properties of the composites [3]. Therefore, it a key factor is to get sufficient infiltration and adhesion between the fibers in the fabric and the matrix resin. As a result, surface treatment of the fiber surface is necessary.

For hollow integrated core sandwich fabric with glass fiber/carbon fiber (GF/CF) hybrid face sheets, the fiber surface modification was different from the ordinary sandwich fabrics. The desired treatment effects were not only for improving the interfacial adhesion between the fibers and the matrix and getting a uniform treatment throughout the fabrics, but also optimizing the interfacial properties of the GF/CF hybrid face sheets. Various surface treatment methods on glass fibers or carbon fibers have been applied by forming polar groups onto the fiber surface and modifying the surface morphology [4-8], such as chemical method [9], electro chemical method [10], and plasma treatment [11]. But research on the fiber surface modification of the hollow integrated core sandwich fabrics with hybrid face sheets has been very limited [12, 13].

In recent years, atmospheric pressure dielectric barrier discharges air plasma (DBDs) technology has been developed as an effective method for fiber surface modification. In this way functional groups (such as hydroxyl, carbonyl, carboxyl groups) can be formed on the fiber surface, which could react with the polymer matrix and improve the adhesion to the surrounding polymer [14,15]. Effects of plasma treatment, including improving the wettability [16,17] and adhesion [18] of the fibers, have been reported. DBDs is a fast, versatile and environmentally-friendly surface modification technique and is especially suitable for the sandwich fabrics. But the effect of plasma treatment could not be maintained for a long time and would decline with time. Thus, a compound surface treatment was applied to overcome this drawback and yield a better compatibility between the fabric and matrix. And the use of coating technique with a silane coupling agent for the second surface modification of integrated sandwich fabric is recommended. It is known that the hydroxyl groups of the silanes and those of the glass fiber or carbon fiber surface can react with each other through siloxane bonding or hydrogen bonding at the interface between the glass fiber or carbon fiber and the silane coupling agent [19]. Thus, the interfacial adhesion can be improved further by this reaction, which indicates the adhesion process of the silane coupling agents onto the glass or carbon fiber surface [20]. Therefore, the optimum condition of composites can be obtained by introducing the silane coupling agent onto the fiber surfaces after the plasma treatment.

The purpose of the present work was to investigate the effect of the compound surface treatment on the mechanical properties of hollow integrated composites with GF/CF hybrid face sheets. Moreover, the effect of the compound surface modification on the tensile strength of glass fibers and carbon fibers was also investigated.

EXPERIMENTAL

Materials

The hollow integrated core sandwich fabric with hybrid face sheets was made by Nanjing Fiberglass R&D Institute. The materials were 3K glass fibers and polyacrylonitrile (PAN) based carbon fibers. And the face sheet was glass/carbon mixed plain woven fabric and the core was glass fibers only. The thickness, warp density and weft density of the face sheet were 0.4 mm, 100 ends/10 cm and 50 ends/10 cm, respectively. The thickness and the warp density of the core were 5 mm and 50 ends/10 cm, respectively. Epoxy resin (E-51), polyamide curing agent (651) and epoxy reactive diluent (660) were supplied by Wuxi Resin Factory of Blue Star New Chemical Materials Co., Ltd. Silane coupling agent (KH-560) and ethanol were provided by Sinopharm Chemical Reagent Co., Ltd. All reagents were used without any further process.

Surface Treatment

First-Step Surface Treatment of Integrated Core Sandwich Fabric

All the integrated core sandwich fabrics were soaked in acetone for one hour and then dried at 60 °C for one hour in a vacuum oven. The atmospheric pressure plasma treatment was performed by using the DBD operating in air. The distance between the nozzle and the specimen was 3 mm and the treated area dimension was about 310 mm × 280 mm. The specimens were fixed on a frame and treated for two minutes under the nozzle for one lap on a conveying belt moving at a constant rate of 3 m/min. Additionally, two sides of the samples were treated under the same conditions, with discharge power of 150 W and frequency of 20 KHz.

Second-Step Surface Treatment of Integrated Core Sandwich Fabric

Considering the drawback of the DBDs technology, the treated integrated core sandwich fabric were dipped into the silane coupling agent solution (1 wt %) immediately for one hour. Then the fabrics were left for about 24 hours at room temperature and dried at 120 °C for two hours in a vacuum oven.

Preparation of Hollow Integrated Core Sandwich Composites

In the current study, all the hollow integrated core sandwich composites were prepared using vacuum assisted resin infusion molding processing. For the preparation of hollow integrated composites, the hollow integrated core sandwich fabric with GF/CF hybrid face sheets was cut to the required size. A flat aluminum plate was used as a mold and the mold surface was cleaned with acetone before the manufacturing process. Two flexible spiral plastic tubes were then placed on the longer sides of the mold for infusing the resin and connecting to vacuum pump. Then entire assembly was vacuum bagged. Fabric perform was laid down on the mold surface and covered by another layer of Teflon release film. Then the epoxy resin was used for infusion under vacuum to wet the fabric perform uniformly and faster as opposed the hand lay-up process. Once the entire fabric perform was uniformly wetted, the vacuum bagging was removed and the vertical pile were allowed to spring back, thus providing the hollow integrated core sandwich architecture. The wetted fabric was cured at 60 °C for five hours and then was transferred to room temperature for 24 h for completely curing. *Figure 1* shows the hollow integrated core sandwich composites at different stages of manufacturing.

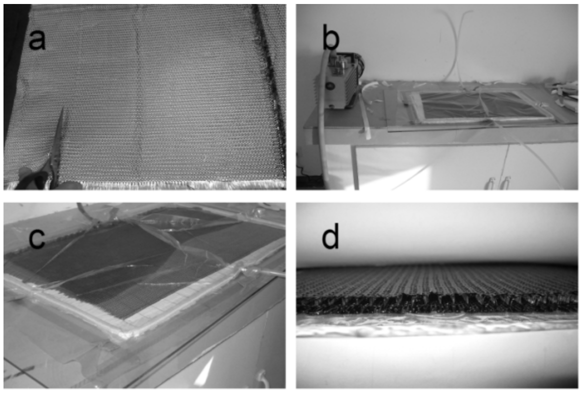


FIGURE 1. Manufacturing process of hollow integrated core sandwich composites at different stages (a) cutting dry fabric (b) vacuum bagging (c) resin infusion (d) curing.

CHARACTERIZATION

The surface chemistry of the fabric was examined by Fourier transform infrared spectrometer (FTIR, 470, Thermo, USA) and the spectra were recorded in air by use of a FTIR Nexus spectrometer. The morphologies of glass fibers and carbon fibers were characterized by scanning electron microscopy (SEM, Quanta-200, FEI, Holand).

TENSILE TEST OF SINGLE FILAMENT

Tensile testing of single filament fixed to a paper frame was carried out by the fiber electronic strength tester (Fiber Electronic Strength Tester, YG001A, Taicang, China) with a gauge length of 10 mm. About 50 specimens were tested and the average value was adopted. Then the tensile strength of the fiber could be calculated according to the following equation:

$$\sigma=F/\pi r^2 \tag{1}$$

where F and r was the maximum value of breaking load (cN) and radius of the fiber (μm), respectively.

MECHANICAL PROPERTIES OF HOLLOW INTEGRATED CORE SANDWICH COMPOSITES

Considering the complex structure of the hollow integrated core sandwich composites, the warp and weft mechanical properties were greatly different. The distinction between the warp direction and weft direction were noticed during the tensile test, bend test and compression test of the hollow integrated core sandwich composites.

TENSILE TEST

According to the GB/T1447-2005 standard of People's Republic of China, tensile tests were performed on a WDW-200 Universal Test Machine (Universal Test Machine, WDW-200, Ruice, China) with a strain rate of 5 mm/min. Specimens were cut into long narrow strips (250 mm × 25 mm × 5 mm). Additionally, aluminum stubs (50 mm× 2.5 mm) were glued to the ends of each strip of composite to make sure that the specimens were not damaged when they were clamped into the test machine. And the tensile strength of the composites were calculated according to the following equation:

$$\sigma_t=\frac{P}{w\times t_f} \tag{2}$$

where P, w and t_f was the fracture load (N), width of the specimen (mm) and thickness of the surface layer (mm), respectively.

BENDING TEST

The three-point bending test was applied to measure the flexural properties of the composites. According to the GA1447-2005 standard of People's Republic of China, the three-point bending test was performed on LRXPLus material test machine (LRXPLus, LLOYD, England). In the three-point bending test, the flexural strength was calculated from

$$\sigma_f=\frac{P\times l}{4b\times t_f\times(h-t_f)} \tag{3}$$

where P and t_f presented the maximum load which exerted on the specimen prior to fracture and the face sheet thickness, respectively; l, b and h were the length, width, thickness of the specimen, respectively.

COMPRESSION TEST

The flatwise compression test was applied to measure the compression performance of the hollow integrated core sandwich composites. According to the GB/T1453-2005 standard of People's Republic of China, the flat compression test was performed on LRXPLus material test machine (LRXPLus, LLOYD, England). This test standard requires a beam specimen of 30 mm ×30 mm ×5 mm for the flat compression test. Like the tensile test, the compression test was also in-plane. And the flat compression strength of the composites was calculated according to the following equation:

$$\sigma = \frac{P}{S} \tag{4}$$

where P and S were the fracture load (N), cross section area of the specimen (mm^2), respectively.

RESULTS AND DISCUSSION

SEM Observations

Scanning electron microscopy was employed to study the physical effects produced on the surfaces of glass fibers and carbon fibers. *Figure 2* shows the SEM images of glass fiber surfaces untreated and treated. As clearly shown in *Figure 2a*, the untreated surface of glass fiber was smooth. After the first-step treatment, there were some uniform prominent grooves and parts on the surface. Moreover, the number and size of the prominent parts on the surface increased after the compound treatment. *Figure 3* shows the SEM images of carbon fiber surfaces untreated and treated. The change of carbon fiber surface was similar to that of glass fiber.

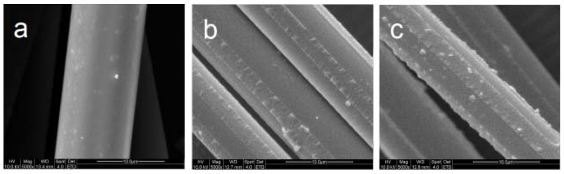


FIGURE 2. SEM images of glass fiber surface (a) untreated (b) after first-step treated (c) after second-step treated.

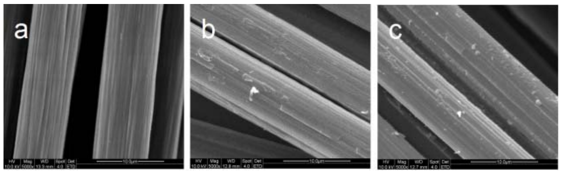


FIGURE 3. SEM images of carbon fiber surface untreated (b) after first-step treated(c) after second-step treated.

FTIR Analysis

To further evaluate the characteristics of the silane coupling agent after it had been immobilized to the glass fiber surface, FTIR spectroscopy was used. Herein, only the FTIR spectra of glass fiber after the DBDs surface treatment and the two-step surface treatment are shown in *Figure 4a*. The spectrum in *Figure 4a* after the DBDs treatment had 3 peaks at 3300 cm^{-1} (-OH group), 1640 cm^{-1} (-C=O group), and 1540 cm^{-1} (-NH group). The peak around 928 cm^{-1} appeared in the spectrum reconfirmed a condensation reaction between Si-OH groups of the silane coupling agent and the hydroxyl groups on surface of the DBDs treated glass fiber as proposed. Additionally, the peaks at 867 cm^{-1} and 856 cm^{-1} assigned to the epoxide group appeared.

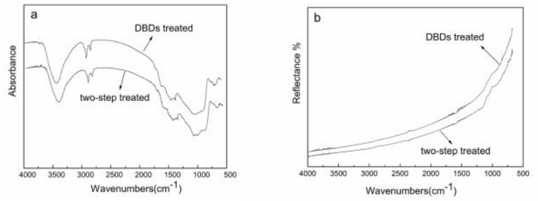


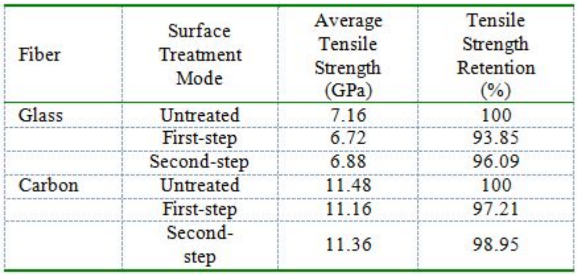
FIGURE 4. FTIR spectra of fabric after surface treatment (a) glass (b) carbon fibers.

Figure 4b shows the FTIR spectra of carbon fiber after the DBDs surface treatment and the two-step surface treatment. Similar to FTIR spectra of the glass fiber, the peaks at 867 cm-1 and 856 cm-1 assigned to the epoxide group appeared. Additionally the peaks at 1090 cm-1 and 1056 cm-1 presented the characteristic peaks of –O-Si-O groups. The above observations indicate that chemical modification on the surface of the carbon fibers occurred after the second-step surface treatment. All these FTIR results confirmed the chemical reactions as designed.

Effect of Two-Step Surface Treatments on Fiber Strength

It is recognized that loss of fiber strength is unavoidable during fiber surface treatment in most cases due to the etching effect [21]. It is necessary that the surface treatment should avoid excessive loss of fiber strength as much as possible in order to ensure excellent overall mechanical performance of the fiber composites [22]. Thus, in the two-step surface treatment, neither surface treatment step should have obvious influence on the strength of both fibers subjected to the surface treatment. The experimental results are listed in *Table I.* As seen from this table, the average tensile strength of glass fibers after the first-step and the second-step treatment decreased by 6.15 % and 3.91 % with respect to the untreated ones. Moreover, the average tensile strength of carbon fibers after the first-step and the second-step treatment decreased by 2.79 % and 1.05 % with respect to the untreated ones. The strength loss was due to the etching which generated some grooves and parts on the fiber surface (shown in *Figure 2 and Figure 3*). Additionally, it was noteworthy that the second-step treatment reinforced the strength loss greatly. These results indicate that the second step was beneficial and recovered some of the strength loss resulting from the first treatment step.

TABLE I. Effect of two-step surface treatment on the tensile strength of fibers.



Fiber	Surface Treatment Mode	Average Tensile Strength (GPa)	Tensile Strength Retention (%)
Glass	Untreated	7.16	100
	First-step	6.72	93.85
	Second-step	6.88	96.09
Carbon	Untreated	11.48	100
	First-step	11.16	97.21
	Second-step	11.36	98.95

Effect of Two-Step Surface Treatment on Composite Tensile Strength

The tensile failure mode of hollow integrated core sandwich composites is different from the general fiber-reinforced composites based on their special structure. And *Figure 5* shows the tensile failure mode of hollow integrated core sandwich composites on the warp and weft directions, respectively. The average tensile strength of hollow integrated core sandwich composites at warp and weft directions after the two-step surface treatment were increased by 14.37 % and 10.54 % with respect to the untreated ones, as shown in *Table II*. It was proven as well that the two-step surface treatment improved the tensile strength of hollow integrated core sandwich composites obviously. Moreover, the tensile strength at the weft direction of hollow integrated core sandwich composites was much higher than the tensile strength at the warp direction. This could be due to its intrinsic structural factor and the addition of carbon fibers at weft direction. As mentioned in Experimental section, the hybrid face sheet was woven with glass fibers (warp direction) and carbon fibers (weft direction). And the carbon fiber hybrid system has a positive impact on the strength properties, as it had been expected.

TABLE II. Effect of two-step surface treatment on the tensile strength of hollow integrated composites in different directions.

Tensile strength	Untreated	Two-step treated	Tensile strength retention (%)
Warp	410.44	469.40	114.37
Weft	906.88	1002.44	110.54

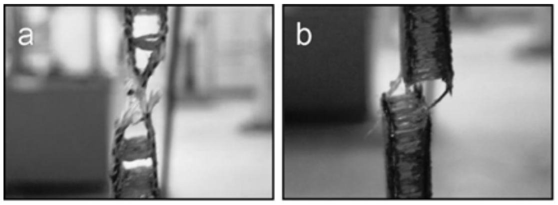


FIGURE 5. Tensile failure mode of hollow integrated composites in (a) warp (b) weft directions.

Bending Performance

Figure 6 shows the failure mode of the bending test of hollow integrated core sandwich composites at warp and weft directions. The figures show that the failure started at the tensile side and the formed crack spread along the line of action of bending. The vertical piles were also cracked along the line of action of bending. This could be due to high contact stress at the load point, which caused the breakage of vertical pile directly under the bending region. Furthermore, the failure on the warp direction (*Figure 6a*) was located in the middle of the core frameworks. This could be due to the lack of resistance points, the thickness of the face sheet and poor compression resistance, which lead to collapsed easily. Meanwhile, there was no obvious collapse phenomenon on the face sheet at the weft direction (*Figure 6b*), due to its compact frameworks, uniform resistance points, and good compression resistance. The different three-point bending failure mode of hollow integrated composites made the bending strength at weft direction much higher than at warp direction.

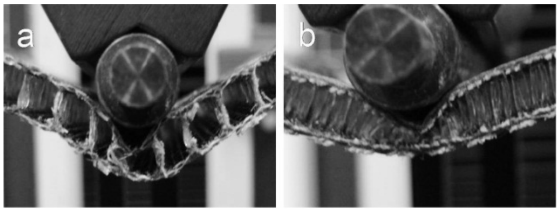


FIGURE 6. Three-point bending failure mode of hollow integrated composites in (a) warp (b) weft directions.

Different directions of load-displacement responses are presented in *Figure 7* and it was observed that all materials underwent a brittle failure. Noticeably, the load-displacement curves of the untreated hollow integrated core sandwich composites obtained in the three-point bending test were much lower than the treated ones. As shown in the graph, the displacement increased linearly with the load at the preliminary stage. And then with increasing load, the top face sheet began to fail and push down to the core materials, followed by complete damage resulting from the load declining sharply. According to Eq. (3), the average tensile strength of hollow integrated core sandwich composites at warp and weft directions after the two-step surface treatment increased by 18.79 % and 14.70 % with respect to the untreated ones. This improvement could be due to the surface modification to the hollow integrated core sandwich fabric with GF/CF hybrid face sheet which lead to increasing the adhesiveness of fabrics to the epoxy resin.

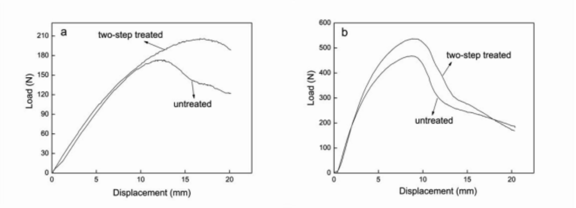


FIGURE 7. Load-displacement curves of three-point bending test on hollow integrated composites in (a) warp (b) weft directions.

Compression Performance

The suitability of the fabric in such composites depends essentially on the surface properties, by which the adhesion between fibers and surrounding matrix is determined. Fiber surface treatment is crucial to the properties of fiber composites, especially the integrated sandwich fabric composites due to their special spring resilience during the wetting-outing process. As shown in *Figure 8*, the average compression load of hollow integrated core sandwich composites after the two-step surface treatment increased greatly compared to the untreated ones. According to Eq. (4), the average compression strength of hollow integrated core sandwich composites after the two-step surface treatment increased by 21.67 % with respect to the untreated ones. The reasons for this improvement could be summarized as follows: (i) etching effect, resulting in the increase of functional groups and contact area, (ii) chemical reaction, resulting in increasing the adhesiveness of fabrics to the epoxy resin.

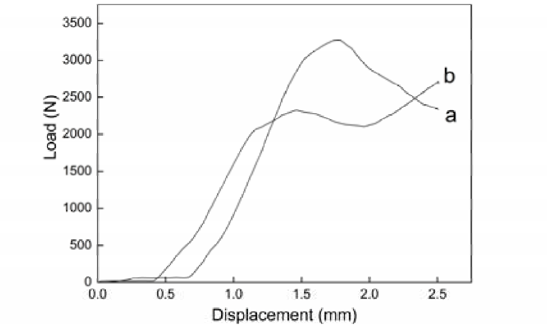


FIGURE 8. Load-displacement curves of flatwise compression test (a) two-step treated (b) untreated.

CONCLUSIONS

In the present study, the two-step surface treatment consisting of atmospheric pressure dielectric barrier discharge (DBDs) air plasma and silane coupling agent coating proved to significantly enhance the mechanical properties of the hollow integrated core sandwich composites with GF/CF hybrid face sheets. The monofilament tensile test suggested that no extra damage was found for the hybrid fibers subjected to the two-step treatment with respect to the first-step treated and the untreated fibers. It was concluded that the two-step surface treatment was an effective way of modifying the surface conditions of the glass/carbon hybrid fibers and improving the performance of their composites. This is of vital importance for hollow integrated core sandwich composites as fabrics are often prepared prior to fiber surface treatment.

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AUTHORS' ADDRESSES

Kejing Yu
Haijian Cao
Kun Qian
Hongshun Li
Juanjuan Wang
Key Laboratory of Eco-textiles, Ministry of Education,
1800 Lihu Road
Wuxi, Jiangsu 214122
CHINA