Effects of plasma treatment on properties of carbon fiber and its reinforced resin composites

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Abstract
The influence of plasma treatment on the wettability of carbon fiber was studied using the vacuum assisted resin transfer molding (VARTM) process. The influence of plasma treatment on the mechanical properties of carbon fiber-reinforced polymer (CFRP) composites, including interlaminar shear strength and tensile properties, were investigated. The carbon fiber surface chemistry analysis was carried out by Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and x-ray photoelectron spectroscopy (XPS). Results showed that low-temperature plasma treatment had little effect on the surface morphology of the carbon fiber; however, it changed the chemical surface state of the carbon fiber, which contributed to enhance the wettability of the carbon fiber by increasing the perfusion speed of the resin to be more than two times of the original speed. The fiber wettability improvements are of great significance to the preparation of the CFRP composite by the VARTM process. Compared to untreated carbon fiber, the plasma treatment caused an acceptable decrease in tensile properties and offered an increase in the interlaminar shear strength of the CFRP composite. Low-temperature plasma treatment played an important role in the effective preparation and application of the CFRP composite.

1. Introduction

Carbon fiber-reinforced polymer (CFRP) composites are a kind of low density and high-performance composite material [1, 2]. It has advantages of fatigue resistance, chemical corrosion resistance, small coefficient of thermal expansion, and low density and is widely used in aerospace, energy, automotive, sports, and other industrial fields [3–5]. In recent time, the worldwide market has required an increased amount of carbon containing composites for various applications [6]. The properties of the CFRP composite are not only dependent on the characteristics of the individual components but also on the preparation process of the CFRP composite. At present, driven by the environmentally friendly policies, eco-friendly molding processes of the CFRP composite have been intensively explored [7–11]. The vacuum assisted resin transfer molding process (VARTM) is a new process developed in recent years to prepare fiber-reinforced resin matrix composites [12–14], which has advantages of stable reliability, high molding efficiency, simple operation, low cost, and environmental protection. It has also been shown to be a good method to prepare fiber-reinforced resin matrix composites [15–17]. However, the carbon fiber has a smooth surface and low chemical activity which makes it difficult to be wetted out by the resin in the VARTM process, and the poor wettability of the fiber can lead to many dry spot defects and low mechanical properties of the composites. Especially when the size of the composite products is large, the resin cannot quickly impregnate the carbon fiber, and the resin cured before the carbon fiber preform was completely wetted. Low molding efficiency seriously affects the quality and efficiency of the composite preparation process, which further affects the application of carbon fiber-reinforced composites. Therefore,
improving the wettability of the carbon fiber is an urgent problem to be solved, and surface modification is a useful approach to solve this issue [18, 19].

Usual surface modification methods include surface oxidation treatment, surface coating treatment [20, 21], γ-ray irradiation [22], supercritical fluid surface treatment [23], and plasma surface modification [24]. There are some defects in the first four surface modification methods. Some can easily damage the fiber and reduce the bulk strength, some are complex to operate, and some are not technically mature. The plasma treatment method has characteristics of high efficiency, low energy consumption, no pollution, simple operation, and low damage to the bulk fiber [25–28], so it is a good method to modify the fiber surface.

In this study, responding to the problem of the poor molding preparation process of the CFRP composite caused by insufficient carbon fiber wettability, the carbon fiber was treated by low-temperature (20 °C–80 °C) air plasma under vacuum conditions, and the influence of different treatment time on the infiltration of carbon fiber was investigated. Moreover, the influence of plasma treatment on the interlaminar shear strength and tensile properties of the CFRP composite were studied. This study optimized the plasma treatment scheme of the carbon fiber, which provides technical support for the effective preparation and application of a CFRP composite by the VARTM process.

2. Experimental section

2.1. Low-temperature air plasma treatment on carbon fibers

The low-temperature air plasma treatments were performed on a plasma processor (SY-D235L) produced by Suzhou OPS Plasma Technology Co., Ltd. There is a sample holder between two sets of radio frequency electrodes in the experimental plasma processor, as shown in figure 1. The carbon fiber fabrics named CK400 provided by Nanjing Fiberglass Research & Design Institute Co. Ltd, China (size: 100 mm × 350 mm, whose strip direction is along the fiber direction) were placed onto the holder where the plasma could have an effect on the carbon fiber surface. The plasma was excited by an inductively coupled radio generator at a frequency of 13.56 MHz. The operating pressure was below 50 Pa, and the power was set at 200 W. During air plasma treatment processing, the air was fed into the vacuum chamber at a flow rate of about 150 sccm. The processing diagram of the carbon fiber in the plasma processor is shown in figure 1.

The carbon fiber fabric strips were treated for different durations in the air plasma atmosphere, namely, 1 min, 3 min, 5 min, 10 min, 15 min, 20 min, 25 min, and 30 min. When the carbon fiber was being treated in the vacuum chamber, it showed purple light emission, observable from the window (figure 1). The corresponding plasma treated carbon fiber types were labelled ck-1, ck-3, ck-5, ck-10, ck-15, ck-20, ck-25, and ck-30, and the untreated carbon fiber fabric strip was labelled ck-0 in this study.

2.2. Wettability characterization

The carbon fiber wettability was characterized by the following procedures: (1) Each untreated monolayer and the plasma-treated carbon fibers were laid on the flat mold in parallel. (2) The untreated and plasma-treated carbon fibers were sealed in one vacuum bag and vacuum-pumped by rotary vane vacuum pump (2X-8, Boshan Chengkun vacuum pump factory, China) to pressures lower than −0.095 MPa. (3) The VARTM process was run at vacuum conditions of −0.095 MPa, where the vinyl ester resin without curing agent perfused into the fibers,
2.3. Composite preparation of vinyl ester resin reinforced by untreated and plasma-treated carbon fibers

Using the VARTM process, the composites of vinyl ester resin reinforced by untreated and plasma-treated carbon fibers were prepared by adding curing agent under vacuum conditions of $-0.095$ MPa. After removing the mold, the composites were transferred into an electro-thermal blast drying box (ZB-III, Shandong Zibo Instrument Factory) for solidification (at $120^\circ$C for 2 h). After natural cooling, the composites were obtained.

2.4. Composite sample preparation and mechanical property characterization

Mechanical properties, including interlaminar shear strength and tensile properties, of the CFRP composites were studied by universal material testing machine (Instron5966, Instron, UK) in this paper. For characterizing interlaminar shear strength, the composite samples made from carbon fibers before and after plasma treatment were prepared, whose thicknesses were 15 mm, according to the GB/T1450.1–2005 standard. Composite samples with thickness of 3 mm were prepared according to the GB/T1447–2005 standard for testing the tensile properties.

2.5. Surface analysis of the carbon fibers before and after plasma treatment

The analysis of the carbon fiber surface chemistry was carried out by Scanning electron microscopy (SEM) (QUANTA 200, FEI, the Netherlands), Fourier transform infrared spectroscopy (FTIR) (Nexus 670, Thermo Nicolet, USA), and x-ray photoelectron spectroscopy (XPS) (Escalab 250, Thermofisher Scientific, USA), which were also used to analyze the changes in carbon fiber wettability before and after plasma treatments.

3. Results and discussion

3.1. Effect of plasma treatment on the wettability of carbon fiber fabrics

The wettability of the carbon fiber fabric studied in this paper refers to the spreading ability on the carbon fiber surface or the tendency of vinyl ester resin to be adsorbed into the carbon fiber. The most common methods to study fiber wettability are contact angle and adsorption methods, however, the testing conditions of the contact angle of the fiber fabric are relatively harsh, and the precision of the test equipment is extremely high. The adsorption method uses the capillary principle to immerse one end of the fiber bundle into the liquid, then record the soaking distance of the liquid in the fiber bundle over a certain period of time to characterize the wettability of the fiber. The adsorption method is intuitive, reliable, and easy to operate, but for black carbon fiber, the position of resin soaking is difficult to visually identify, so it is necessary to add color to the resin for identification. The addition of color materials will affect the surface activity of the resin and then affect the real perfusion of the vinyl ester resin in the fiber fabric. To study the wettability of the carbon fiber fabric, VARTM...
technology was used in this study. The wettability of the carbon fiber was characterized by testing the perfusion velocity of the vinyl ester resin into the carbon fiber fabric.

Under vacuum, the greater the flow speed of the resin, the stronger the carbon fiber wettability. Figure 2 shows the relationship between the perfusion distance and perfusion time of vinyl ester resin in carbon fiber fabric under different treatment times. A picture of the untreated and plasma-treated carbon fiber fabric perfused by vinyl ester resin is presented in figure 3. It can be seen from figure 2 that the plasma treatment time can seriously affect the wettability of the carbon fiber. For the same perfusion distance, the perfusion time that the vinyl ester resin perfused into the treated carbon fiber fabric is much shorter than that in the untreated fabric. This means that it is easier for the resin to perfuse the plasma-treated carbon fiber.

Table 1 provides the average perfusion speed of resin at different perfusion distances. Due to the effects of perfusion resistance, with increased perfusion distance, the resin’s perfusion speed will be slower in the same carbon fiber fabric sample, which is in line with Darcy’s law [29]. However, after the carbon fiber fabrics were treated by plasma, the flow speed of the resin perfusion can increase to more than twice the original carbon fiber. It is observed that when the carbon fiber fabrics are treated for 5~30 min, the perfusion speed of the resin is increased by more than three times of the original, and the wettability of the carbon fiber is significantly improved. For example, the samples of ck-5, ck-25, and ck-30. It is also noticed that when the treatment time is enough (≥5 min), there is no distinct change in the wettability among the plasma treated carbon fibers, as shown in table 1.

It can be concluded from the above analysis that low-temperature plasma treatment can significantly improve the wettability of the carbon fiber. When the carbon fibers are processed with enough plasma treatment time (≥5 min in this study), the wettability of the fibers was obviously improved. The improvement in carbon fiber wettability can effectively improve the operability of the VARTM process for the preparation of the CFRP composite, which is significant for the promotion and application of the CFRP composite.

3.2. SEM analysis
The surface morphology of carbon fibers before and after plasma treatment at different times were analyzed by SEM, as shown in figure 4. From the SEM of figure 4, before and after plasma treatment, the surface morphology of carbon fiber had no obvious changes, which shows that low-temperature plasma treatment could not enhance
the roughness of the carbon fiber surface. This test result is different from other plasma treatment reports [30, 31]. With slight surface effects within 30 min of plasma treatment, there was no distinct physical damage caused to the carbon fiber body. Therefore, the carbon fiber wettability improvements in this paper were not primarily caused by fiber surface roughness.

In previous works, it was reported that oxygen plasma treatment can introduce polar functional groups onto the fiber surface [32], which confirms that the improvement in carbon fiber wettability is related to changes in the chemical state of the carbon fiber surface after plasma treatment.

3.3. Fourier transform infrared spectroscopy (FTIR) analysis
Figure 5 shows the FTIR spectra of carbon fiber before and after plasma treatments. It can be seen from the spectrum that after the plasma treatment, there were more \(-\text{C}–\text{H}\) bond absorptions at the 2850 cm\(^{-1}\) and 2923 cm\(^{-1}\) peaks of the FTIR spectra, which indicated that the polar \(-\text{C}–\text{H}\) bond could be produced in the treatment of carbon fiber by plasma treatment. In addition, the carbon fiber treated by plasma showed an obvious O=\text{C}=\text{O} characteristic peak at 2341 cm\(^{-1}\), and the intensity of the O=\text{C}=\text{O} characteristic peak correspondingly increased when treated for 5 min and 30 min. Additionally, a weak aldehyde peak appeared at 1750 cm\(^{-1}\). It could be concluded that more polar groups and oxygen-containing groups were introduced on the surface of carbon fiber after plasma treatment, which enhanced the surface activity so as to improve the wettability of the carbon fiber.

3.4. X-ray photoelectron spectroscopy (XPS) analysis
Figure 6 is the complete XPS spectrum of the carbon fibers before and after low-temperature plasma treatment for 5 min. It can be seen from figure 6 that the peak shapes of O1s and C1s in the XPS spectra of the carbon fiber slightly changed after plasma treatment for 5 min. It indicates that plasma treatment could cause slight changes of the carbon and oxygen groups on the surface of the carbon fiber.

Figure 7 shows the C-spectrum and O-spectrum analysis of the carbon fiber before and after plasma treatments. It could be seen from figure 7(a) that after being treated by low-temperature plasma for 5 min, the C-spectrum of the carbon fiber moved to the direction of high binding energy, indicating that some C-groups in the carbon fiber after plasma treatment changed from a low-energy state to a high-energy state. Figure 7(b) demonstrates a different change from the C-spectrum, where the O-spectrum moved towards the direction of low binding energy, and the O\(_2\) introduced from the treatment air formed low-energy O-groups on the surface.
Figure 5. The FTIR spectrum of carbon fiber before and after plasma treatment.

Figure 6. XPS analysis of the carbon fibers before and after plasma treatment.

Figure 7. The C-spectrum (a) And O-spectrum (b) Of the carbon fibers before and after plasma treatment.
of the carbon fiber, which contributed more to enhance the surface activity of the carbon fiber. These results support that the chemical state of the fiber surface gets changed when treated with plasma. Considering the fact that the plasma could affect the fiber surface in the depth of within several hundred Å [33], so the influence of plasma treatment on the fiber surface is limited. Combining with the wettability tests (table 1), we can presume that the chemical state of the fiber surface with plasma treatment time more than 5 min is changed obviously and nearly completely. This is the reason that the wettability of the carbon fiber shows no distinct difference when being treated by plasma with times longer than 5 min (table 1).

For better verification, the C-spectrum peaks of the carbon fiber before and after plasms treatment are analyzed. It can be seen from figure 8(a) that there are four peaks in the C-spectrum before plasma treatment, and five obvious peaks (figure 8(b)) in the C-spectrum after plasma treatment for 5 min. There is a new peak at binding energy of 290.0 eV (CO$_3^{2-}$) after plasma treatment, indicating that there is plasma oxygen on the carbon fiber surface. Plasma oxygen can easily react with materials on the fiber surface, which can effectively improve the surface activity and enhanced the wettability of the carbon fiber.

3.5. Effect of plasma treatment on the interlaminar shear strength of the CFRP composites

The interfacial adhesion properties between carbon fiber and resin is the main factor affecting the interlaminar shear strength of the CFRP composite. It can be seen from figure 9 that the interlaminar shear strength of the CFRP composite increases significantly after the carbon fiber was plasma-treated. In the range of 1–30 min, with increasing treatment time, the interlaminar shear strength of the CFRP composite increases first and then decreases, with overall increases of 5.2%–15.4%. When the treatment time is 15 min, the interlaminar shear strength of the CFRP composites is the highest, reaching 30.6 MPa, which is an increase of 15.4%. When the
treatment time was 30 min, the interlaminar shear strength of the CFRP composites was the lowest, 27.8 MPa, which was an increase of 5.2%. It can be seen that plasma treatment on the carbon fiber can improve the interfacial adhesion properties between fiber and resin by improving the surface polarity and reactivity, which has been proven to be an effective method for enhancing interlaminar shear strength of the CFRP composites.

3.6. Effect of plasma treatment on the tensile properties of the CFRP composite
Tensile properties are important parameters to reflect the mechanical properties of CFRP composites. Figure 10 shows the influence of plasma treatment on the tensile properties of a CFRP composite. It can be seen from figure 10 that after the carbon fiber was treated with plasma, the tensile properties of the CFRP composite decreased. In the first 5 min, the longer the plasma treatment time, the greater the decrease in tensile properties. When the carbon fiber was treated for 5 min, the tensile strength and modulus of the CFRP composite decreased by 8.3% and 7.0%, respectively. The tensile properties of the CFRP composites are mainly contributed from the carbon fibers. Therefore, the decrease of tensile strength and tensile modulus of CFRP composite should be related to the decrease of fiber tensile strength after plasma treatment. As reported that the tensile strength of the plasma treated carbon fiber decreased from (3.91 ± 0.72) GPa to (1.75 ± 1.37) GPa when compared to the untreated carbon fiber (the plasma treatment time is 16 min) [25]. With increased plasma treatment time, the tensile properties of the CFRP composite negligibly changed in the range of 5–30 min. It is not difficult to understand that in the first 5 min, the plasma treatment on the carbon fiber is gradually deepened from the outside to the inside, but after 5 min, the treated fiber surface blocks further plasma treatment deeper in the fiber, so the tensile properties of the CFRP composite significantly change in the first 5 min and tend to stabilize with more treatment.

According to the drawing process characteristics of the composite tensile test, the tensile properties of the composite are related to the strength of the carbon fiber and the interfacial adhesion with the resin. Another important conclusion in M O H Gioff’s report [34] indicates that the tensile strength of composites is related to fiber volume fraction, and as fiber volume content increases, tensile properties also increase. After a comprehensive analysis of the influence of plasma treatment on carbon fiber in this study, it is concluded that plasma treatment caused the fiber surface state change which led to the decrease in fiber volume content and further caused the decrease in tensile properties of the CFRP composite. This needs to be further studied in future work.

4. Conclusions
It can be concluded that low-temperature plasma treatment can change the chemical state of the carbon fiber surface without damaging the carbon fiber body itself. Under experimental conditions of an air flow rate of 150 sccm and discharge power of 200 W, low-temperature plasma treatment can significantly improve carbon fiber wettability. After the carbon fiber fabric is treated with plasma for 1–30 min, the perfusion speed of the resin could be increased to more than twice that of the original carbon fiber. With the increasing treatment time, the interlaminar shear strength of the CFRP composite increased first and then decreased. When the treatment time is 15 min, the interlaminar shear strength of the CFRP composites is the highest, reaching 30.6 MPa and showing an increase of 15.4%. When the treatment time is 30 min, the interlaminar shear strength of the CFRP
composites is the lowest, being on the order of 27.8 MPa, increased by 5.2%. Additionally, the tensile strength and tensile modulus of the CFRP composites after low-temperature plasma treatment decrease by less than 8.3% and 7.0%, respectively. When the treatment time is longer than 5 min, the tensile properties of the CFRP composite tend to keep stable. These results confirm that plasma treatment is an effective way to prepare CFRP composites by the VARTM process and provides great technical support for the application of CFRP composites.

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**References**

[1] Qian X, Zhang Y G, Wang X F, Heng Y J and Zhi J H 2016 *Surf. Interface Anal.* 48 1271–7
[2] Fan H C, Gu Y Z, Wang S K, Li M and Zhang Z G 2018 *Polym. Compos.* 39 E2529–39
[3] Hsieh T H, Huang Y S, Wang F X and Shen M Y 2018 *Composite Structures* 206 628–38
[4] Seda H, Meral C and Ayse A 2018 *J. Appl. Polym. Sci.* 135 46881
[5] Zhang Y N, Xu F J, Zhang C Y, Wang J, Jia Z M, David H and Qiu Y P 2016 *Compos. Part B Eng.* 99 358–65
[6] Mattia B, Carlo R, Mauro G, Massimo R, Pravin J, Alberto T, Michael C and David C B 2019 *J. Appl. Polym. Sci.* 137 48896
[7] Margherita B, Mario P, Marta T, Giovanni D, Stefano T, Michele M and Mirko S 2016 *Sol. Energy Mater. Sol. Cells* 155 436–45
[8] Bancora S P, Binetruy C, Advani S G, Syerko E and Comas-Cardona S 2018 *Composites Part A* 113 359–69
[9] Nevin G K, Ayse A and Veli D 2012 *J. Reinif. Plast. Comp.* 31 1053–60
[10] Yin X C, Yin Y H, Feng Y H, Zhang G Z and Wen J S 2018 *Adv. Polym. Technol.* 37 3861–72
[11] Wongsriraksa P and Nakaib A 2019 *Adv. Polym. Technol.* 38 177–85
[12] Pavel S and Suresh G A 2018 *Int. J. Mater. Form.* 11 503–15
[13] Jia L X, Tian F, Liu J M, Yan R S and Pan J 2018 *Mater. Sci. Eng.*, Part A 75 39–46
[14] Xue S Z, Peter S and Julien I 2016 *Composites: Part A* 90 371–9
[15] Chung H P, Aurelie L, Abdelghani S, Joel B and Woon I I 2011 *Compos: Appl. Sci. Manuf.* 42 658–68
[16] Keller A, Dransfeld C and Masania K 2018 *Composites Part B* 153 167–75
[17] Amirkhosravi M, Pishvar M and Cengiz A M 2018 *Composites Part A* 114 398–406
[18] Fouzi A, Thomas D, Piera B, Anne Z, Eliane A, Fiorenza F and Constantin V 2016 *Surf. Coat. Technol.* 308 62–9
[19] Jiao W W, Liu W B, Yang F, Jiang L, Jiao W C and Wang R G 2017 *J. Mater. Sci.* 52 13812–28
[20] Chen J T, Shen C H, Yang S D, Masud R and Ma P C 2017 *Comp. Comm.* 4 10–5
[21] Viktor M 2012 *Constr. Build. Mater.* 31 94–104
[22] Qiu Q Y, Xin S L, Xiao I Y, Zeng J C and Wang Z 2006 *Materails Review* 20 436–9
[23] Nikos K, Anastasios C M, Panagiotis N P, Faidonas P, Lamprini S, Dimitrios T, Kostas P, George A and Costas G 2018 *Compos. Sci. Technol.* 157 178–84
[24] Arjunan S, Gurusamy S and Carmen S R 2016 *Mater. Res. Express* 3 095302
[25] Judith M, Elisabeth L, Mario L, Christina K, Michael G, Klaus R and Siegfried H 2018 *Appl. Surf. Sci.* 453 141–52
[26] Lin F B, Li W, Tang Y S, Shao H Q, Su C L, Jiang J H and Chen N I 2018 *Polymers* 10 693
[27] Kai S, Matthias L, Marco L, Maik F, Simone H, Marko B, Christof S and Viktor M 2017 *Materials* 10 360
[28] Meysam B B, Mahmoud S, Ehsanollah N S and Aminoddin H 2016 *J. Adhes. Sci. Technol.* 30 2372–82
[29] Jahn O, W and Steinar E 2018 *J. Biomater.* 18 22–35
[30] Li S, Han K Q, Rong H P, Li X Z and Yu M H 2014 *J. Appl. Polym. Sci.* 131 40250
[31] Liu D, Chen P, Chen M X and Liu Z 2012 *Mater. Sci. Eng.*, Part A 532 78–83
[32] Wang L, Chen P, Xiong X H, Jia C X, Yu Q and Ma K M 2017 *Surf. Interface Anal.* 49 788–93
[33] Liu W D, Chen T T, Xie T S, Lai F W and Qiu R H 2015 *Holzforschung* 69 449–55
[34] Maria O H C, Herman V, Rodrigo H and Luigi A 2005 *Composites Part A* 36 615–23