Study on the Interfacial Shear Strength of a Polyamide 66/Epoxy Resin Composite

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Abstract. In this work, the interfacial shear strength (IFSS) of polyamide 66/epoxy resin composite was improved through the surface modification of polyamide 66 by low-temperature oxygen and nitrogen plasma. Microbond test was used to study the IFSS of the composite. In addition, the composition, microstructures and deboned morphology of the fiber were investigated using the methods of XPS, AFM and SEM. The results show that the polar functional group, such as \(-\text{NH}_2\), \(-\text{COOH}\), and \(-\text{OH}\), were successfully introduced on the surface of the polyamide 66 fiber by plasma treatment. Meanwhile, the surface roughness of the polyamide 66 also increased. After oxygen and nitrogen plasma treatment, the interfacial shear strength of the composite increased to 3.52 MPa and 4.89 MPa, respectively, which is 2 times and 3 times higher than that of the untreated composite. Nitrogen plasma treatment showed better results than oxygen plasma treatment.

1. Introduction
Polyamide 66 fiber plays an important role in composites because of its high fracture strength, wear resistance, good fatigue resistance and low density [1-5]. However, the surface of polyamide 66 fiber is smooth and chemical inertia, which leads to a poor adhesion between the fiber and matrix resin [6-8]. In light of this phenomenon, coupling agents are often used to enhance adhesion in the polyamide 66 fiber-reinforced composite [9-11]. The effects of this traditional method are limited. Its strength still cannot meet requirements for aviation, spaceflight, high-voltage equipment, etc.

In this work, low-temperature plasma treatment was carried out to improve the chemical activity of polyamide 66 in order to enhance the interfacial shear strength between polyamide 66 fiber and epoxy resin. After the low-temperature plasma treatment, polar groups can be introduced on the treated fiber [12-15]. Meanwhile, the roughness of the fiber can also increase due to slight etching [16-18]. The IFSS of the polyamide 66 and epoxy resin was characterized using microbond testing. XPS, AFM and SEM were used to investigate the composition, microstructure and the deboned morphology of the fiber. The results provide a theoretical basis for interfacial adhesion of polyamide 66 fiber reinforced composites.

2. Formatting the Title, Authors and Affiliations

2.1. Materials
Polyamide 66 fiber (used in microbond testing and XPS surface chemical analysis) and film (used in AFM surface morphology analysis) were supplied from Haining Gaobo Special Fiber Co., Ltd., China. The average diameter of the fiber was 0.17 mm, and the thickness of the film is 5 mm. Epoxy resin is...
provided by Nantong Xingchen Synthetic Material Co., Ltd., China. The hardening agent selected in this work is ethidene diamine. The resin and its hardener were mixed at a volume ratio of 100:6. The resin was cured at room temperature for 12 h then post-cured at 60 °C for 4 h.

2.2. Fiber Surface Modification
The polyamide 66 fiber was washed with acetone solution using an ultrasonicator for 10 min, rinsed with fresh deionized water to remove the acetone, and then dried in a vacuum oven at 50 °C.

The cleaned fibers were treated with oxygen plasma and nitrogen plasma using a low-temperature plasma torch (PM-V82, Shenzhen Fang Rui Technology Co., Ltd., China). The power of the plasma torch was 50 W. The gas flow rate was 1.5 kgf/cm². The processing time was 30 s.

2.3. Characterization
Microbond testing was used to characterize the IFSS of polyamide 66 and the epoxy resin. Every sample was observed with an optical microscope. The unqualified samples were removed. The microbond samples were examined using a universal testing machine (Chengde Jinjian Testing Instrument Co., Ltd., China). The displacement rate was 0.5 mm / min. The IFSS was calculated according to the following equation:

$$\tau = \frac{F_m}{A} = \frac{F_m}{\pi \cdot d_f \cdot l_e}$$  \hspace{1cm} (1)

where A is the fiber cross area, Fm is the maximum interfacial shear force, df is the fiber diameter, and le is the embedded fiber length. After testing, the debonded fibers were observed by SEM.

X-ray photoelectron spectroscopy (XPS, AXISULTRA, Kratos, UK) was used to study the chemical structures on the surface of the treated fiber. Atomic force microscopy (AFM, Dimension Icon) was used to observe and test the surface morphology and roughness of the fiber.

3. Results and Discussion

3.1. Interfacial Shear Strength
Figure 1 shows the curve of the relation between the maximum interfacial shear force (Fm) and the embedded fiber length (le) for the control sample and samples treated with oxygen plasma and nitrogen plasma. On the premise of maximizing the regression coefficient, the data in Figure 1 were fitted by a linear function. The slope of the linear function, viewed as the value of Fm/le, were put into equation (1) to calculate the value of the IFSS. This computation can effectively avoid influences of the geometry size of the sample, especially the embedded length (le), on the computed results.

Table 1 shows the computed results of the IFSS. After oxygen plasma treatment, the IFSS of the composite reached 3.52 MPa, which is 3 times greater than that of the control. By contrast, after nitrogen plasma treatment, the IFSS reached 4.89 MPa, which is 39% higher than that of the sample treated by oxygen plasma. This indicates that nitrogen plasma treatment shows better results than oxygen plasma treatment.

3.2. Surface Morphology of the Deboned Fiber
Figure 2 is the SEM micrograph of the deboned fiber. The control fiber (Figure 2(a)) shows a smooth surface. In addition, no residue resin if left on the fiber surface. In Figure 2 (b) and (c), some residual resin was observed around the deboned area of the oxygen plasma treated and nitrogen plasma treated fiber. This shows that the interfacial shear strength is efficiently enhanced by oxygen plasma and nitrogen plasma treatment.
Figure 1. Curves of the relation between the maximum interfacial shear force ($F_m$) and the embedded fiber length ($l_e$): (a) control fiber, (b) oxygen plasma treated fiber, (c) nitrogen plasma treated fiber.

Table 1. The average IFSS of the samples.

| Sample               | IFSS/MPa |
|----------------------|----------|
| Control              | 1.16     |
| Oxygen plasma        | 3.52     |
| Nitrogen plasma      | 4.89     |

Figure 2. SEM micrographs of the deboned fibers: (a) control fiber, (b) oxygen plasma treated fiber, (c) nitrogen plasma treated fiber.

3.3. XPS

Figure 3 shows the XPS survey spectra of the control, oxygen plasma treated and nitrogen plasma treated fiber. C, N, and O elements are present in each survey spectra. The elemental compositions are shown in Table 2. On the surface of the control fiber, the major element is C, by up to 80.38%. The ratio of O/C and N/C is 0.21 and 0.032, respectively.

After the plasma treatment, the elemental composition has an obvious change. The content of O and N elements increased. The ratio of O/C and N/C of the oxygen plasma treated fiber increased to 0.47 and 0.12, respectively. Meanwhile, those of the nitrogen plasma treated fiber increased to 0.54 and 0.19.

Figure 4 is the C1s high-resolution spectra of the control, oxygen plasma treated and nitrogen plasma treated fiber. Curve fitting of the C1s peaks was used to quantify the surface functionality of the fiber. Table 3 lists the content of the functional groups.

In Figure 4 (a), C–C (285 eV), C(=O)NH (285.61 eV), CNH(=O) (286.5 eV) and C=O (288.02 eV) groups were detected on the surface of the control fiber. The content of C(=O)NH groups, which can directly react with the epoxy resin, was only 5%. After the low-temperature plasma treatment, obvious changes had taken place in the groups on the fiber. For the surface of the oxygen plasma treated fiber, the content of C(=O)NH was reduced from 12% to 9%. The content of C=O groups was increased from 3% to 33%. The content of CNH/C=O–C/H groups reached 6%. Meanwhile, few C(=O)=O groups (4%) were detected on the surface of the oxygen plasma treated fiber. On the
nitrogen plasma treated fiber, the content of C(C=O)NH, CNH/C-O-C/H, and C=O groups was 6%, 15% and 33%, respectively. The content of newly introduced C(C=O)-O groups was 5%.

![Figure 3](image-url)

Figure 3. XPS survey spectra of the control, oxygen plasma treated and nitrogen plasma treated fiber.

| Sample                  | Content (%) | C    | N    | O    |
|-------------------------|-------------|------|------|------|
| Control                 | 80.38       | 2.62 | 17.00|
| Oxygen plasma           | 62.90       | 7.54 | 29.56|
| Nitrogen plasma         | 57.70       | 11.15| 31.18|

The above analysis shows that low-temperature plasma treatment can effectively and successfully introduce polar groups, such as -NH$_2$, -COOH, and -OH, on the polyamide 66 fiber. These polar groups can directly react with the matrix resin to form chemical bonds at the interface, improving the interfacial adhesion of the composite. The cause of this phenomenon is that during treatment, molecules in the air and can become active particles by absorbing radiation from the plasma or impacting with the plasma. Meanwhile, the high-energy plasma particles can break chemical bonds on the fiber surface by strongly impacting the surface. The broken bonds will rapidly recombine with the plasma particles or active particles, introducing a mass of polar groups onto the fiber surface.

![Figure 4](image-url)

Figure 4. C1s high-resolution spectra of the fibers: (a) control fiber, (b) oxygen plasma treated fiber, (c) nitrogen plasma treated fiber.

| Sample         | C-C | C(C=O)NH | CNH/C-O-C/H | C=O | C(C=O)-O |
|----------------|-----|----------|-------------|-----|----------|
| Control        | 80  | 12       | 5           | 3   | 0        |
| Oxygen plasma  | 48  | 9        | 6           | 33  | 4        |
| Nitrogen plasma| 42  | 6        | 15          | 33  | 5        |
3.4. AFM
AFM was used to characterize etching by the oxygen and nitrogen plasma on polyamide 66 by observing and testing the surface morphology and roughness of the fiber. Figure 5 shows the surface morphology of the control, oxygen plasma treated and nitrogen plasma treated film. Table 4 is the measured surface roughness. Due to the high energy of the plasma, the carbon on the fiber surface can be oxidized to CO2, making the smooth surface rough. The roughness of the polyamide film increased from 8.67±1.86 nm to 20.51±1.47 nm and 20.49±1.33 nm after oxygen and nitrogen plasma treatment, respectively. The increasing roughness can effectively expand the contact area between the fiber and matrix resin, improving the interfacial shear strength of the composite.

![Figure 5. Surface morphology of the polyamide 66 films: (a) control film, (b) oxygen plasma treated film, (c) nitrogen plasma treated film.](image)

| Sample            | Ra roughness (nm) | Average Ra roughness (nm) |
|-------------------|-------------------|---------------------------|
| Control           | 6.81              | 10.53                     | 8.66                     | 8.67±1.86 |
| Oxygen plasma     | 21.23             | 18.81                     | 21.48                     | 20.51±1.47 |
| Nitrogen plasma   | 19.61             | 19.85                     | 22.02                     | 20.49±1.33 |

4. Conclusions
Oxygen and nitrogen plasma were used to modify polyamide 66 fiber to improve the interfacial shear strength of the polyamide 66 fiber/epoxy resin composite. Microbond testing was used to study the IFSS of composite. The composition, microstructure and deboned morphology of the fiber were investigated using the methods of XPS, AFM and SEM. The results show that polar groups, such as -NH2, -OH, and -COOH, were effectively and successfully introduced on the polyamide 66 fiber after oxygen and nitrogen plasma treatment. The number of polar groups on the nitrogen plasma treated fiber was higher than that on the oxygen plasma treated fiber. Meanwhile, the surface of polyamide 66 was etched, increasing its roughness. Through enhancing the chemical activity of the fiber and expanding the contact area between the fiber and matrix resin, the IFSS of the polyamide 66 fiber/epoxy resin composite increased from 1.16 MPa to 3.52 MPa and 4.89 MPa after oxygen and nitrogen plasma treatment, respectively. Nitrogen plasma treatment showed better results than oxygen plasma treatment.

5. Acknowledgments
The authors acknowledge financial support from the integrated project of Science and Technology of Shaanxi Province, China (No 2014SZ09-Z01); the project of Material Corrosion and Protection Key Laboratory of Sichuan Province (No.2014CL02); the Key Science-Technology Project of Shaanxi Province, China (No. 2014K08-38); and Excellent Doctor Degree Dissertation Research Foundation of Xi’an University of Technology.
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