Atmospheric Pressure Air Plasma In-line Modification of Continuous Fibers (Postprint)

Authors: Jia Caixia, Chen Ping, Wang Qian, Wang Jing, Ren Rong

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Abstract

Three types of high-performance continuous fibers—PBO, Armos, and Twaron—were subjected to in-line modification treatment using atmospheric air dielectric barrier discharge (DBD) plasma technology. The changes in fiber chemical composition, physical morphology and roughness, tensile properties, and interfacial bonding properties of fiber-reinforced composites were comparatively analyzed using X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), atomic force microscopy (AFM), single-filament tensile strength (SFTS), and interlaminar shear strength (ILSS) measurements. The results indicate that after DBD modification, the oxygen and nitrogen element contents on the surface of the three fibers and their surface roughness all increased, and the ILSS of their reinforced composites improved by 18.6%, 10.2%, and 24.8%, respectively. However, the degree of increase in surface oxygen and nitrogen content and the extent of etching exhibited significant differences among the three fibers. This may be related to the molecular structure and thermal stability of the fibers, which collectively influenced the improvement of interfacial bonding properties of composites by DBD treatment. Simultaneously, under plasma treatment conditions where significant improvements in fiber surface and composite interfacial properties were achieved, no significant decrease in fiber SFTS was observed.

Full Text

Preamble

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On-line Modification of Continuous Fibers by Atmospheric Air Plasma*

JIA Caixia[1], CHEN Ping[1,2,**], WANG Qian[2], WANG Jing[1], REN Rong[1]

[1]Liaoning Key Laboratory of Advanced Polymer Matrix Composites Manufacturing Technology, Shenyang Aerospace University, Shenyang 110136, China
[2]Key Laboratory of Materials Modification by Laser, Ion and Electron Beams (Ministry of Education) & School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China

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**To whom correspondence should be addressed, Tel: (024)89723970, E-mail: chenping_{898}@126.com.

Abstract

Three high-performance continuous fibers—PBO, Armos, and Twaron—were subjected to on-line modification using atmospheric air dielectric barrier discharge (DBD) plasma technology. The modified fibers were characterized by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), atomic force microscopy (AFM), single fiber tensile strength (SFTS) measurements, and interlaminar shear strength (ILSS) tests to evaluate changes in surface chemical composition, physical morphology and roughness, tensile properties, and interfacial adhesion of fiber-reinforced composites. Results demonstrated that after DBD modification, the oxygen and nitrogen content and surface roughness of all three fiber types increased, with corresponding ILSS improvements of 18.6%, 10.2%, and 24.8%, respectively. However, significant differences were observed in the degree of oxygen/nitrogen content increase and etching effects among the three fibers, likely related to their molecular composition and thermal stability, which collectively influenced the DBD treatment' s effectiveness on composite interfacial bonding. Importantly, under plasma treatment conditions that significantly improved surface and interfacial properties, the fibers' SFTS showed no substantial degradation.

Keywords: organic polymer materials, on-line modification, atmospheric air plasma, surface, interface
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1. Introduction

PBO fiber (produced by Toyobo, Japan), Armos fiber (produced by "Tverchimovolokno" J.-S. Co., Russia), and Twaron fiber (produced by Akzo Nobel, Netherlands) are high-performance organic fibers. Due to their unique molecular structures, these fibers exhibit high specific strength and modulus, excellent creep resistance, chemical stability, and thermal stability, making them ideal reinforcement materials for advanced polymer matrix composites with broad application prospects in aerospace, defense, and weaponry fields [1-5]. However, these organic fibers possess high molecular crystallinity and highly oriented molecular chains, resulting in smooth surfaces with few polar functional groups and chemical inertness. This prevents the formation of strong chemical bonding and physical anchoring with resin matrices, leading to poor interfacial adhesion that ultimately compromises the overall performance of fiber-reinforced composites. Therefore, selecting appropriate methods for fiber surface modification to enhance bonding strength with resin matrices is essential [6, 7].

In recent years, low-temperature plasma technology has developed rapidly as an efficient, energy-saving, and environmentally friendly approach. Due to its unrestricted generation conditions, suitability for samples of various geometries, and flexibility in selecting different treatment atmospheres, it has become a commonly used fiber surface modification technique [8-11]. Low-temperature plasma can be generated under low-pressure or atmospheric conditions. However, low-pressure plasma typically requires expensive vacuum systems, involves high costs, and is unsuitable for continuous operations. Consequently, atmospheric-pressure low-temperature plasma has attracted increasing attention. Dielectric barrier discharge (DBD), a discharge mode capable of generating stable low-temperature plasma in air at atmospheric pressure, operates without vacuum systems and is not limited by enclosed discharge spaces. It offers convenient processing of samples of any size, low cost, high efficiency, and continuous operation capability, making it highly suitable for large-scale industrial production and widely applied in continuous fiber surface modification [12-16].

This study employed atmospheric air DBD plasma for on-line modification of three commercial high-performance continuous fibers—PBO, Armos, and Twaron. The changes in chemical composition, physical morphology, tensile strength, and interfacial adhesion properties of fiber-reinforced composites before and after plasma treatment were comparatively analyzed, and the differences in DBD modification effects among the three fiber types were investigated.

2. Experimental

2.1 Materials

The three high-performance continuous fibers used in the experiments were PBO, Armos, and Twaron fibers, with their structures and properties listed in . The resin matrix was poly(aryl ether sulfone ketone) (PPESK) thermoplastic resin containing phthalazinone-biphenyl structure. Solvents included acetone (boiling point 56°C) and N,N-dimethylacetamide (DMAc, boiling point 165°C).

2.2 Sample Preparation

[Figure 1: see original paper] presents a schematic diagram of the dielectric barrier discharge (DBD) plasma treatment process and continuous fiber-reinforced composite preparation. When high-voltage alternating current is applied, macroscopically uniform and stable filamentary discharge occurs in the region between the upper and lower electrodes. Fibers cleaned with acetone pass through this discharge gap for plasma treatment, then continuously travel through an impregnation tank containing PPESK/DMAc resin solution. After scraping, winding, and drying, unidirectional prepregs are formed, which are subsequently processed into composite unidirectional panels using high-temperature molding [17]. Since the plasma apparatus remains open to the atmosphere throughout the process, it is suitable for continuous operation and can be termed atmospheric air DBD plasma on-line modification. Detailed technical process parameters are listed in .

2.3 Characterization

Surface chemical composition of fibers was analyzed using an ESCALAB 250 X-ray photoelectron spectrometer (XPS) with a monochromatic Al Kα X-ray source (hv = 1486.6 eV). The vacuum in the analysis chamber was better than 3.0×10^{-10} kPa, with excitation voltage and power of 15 kV and 150 W, respectively. Quantitative analysis of C, O, and N elements employed pass energies of 100 eV and 1 eV step sizes.

Fiber surface morphology was observed using a QUANTA 200 scanning electron microscope (SEM) in low-vacuum mode (60 Pa) at an accelerating voltage of 25 kV.

Surface roughness was measured using a PicoScanTM 2500 atomic force microscope (AFM) in tapping mode. Scanning was performed with Si probes (spring constant 42 N/m, resonant frequency 300 kHz, tip radius $< 10^{-9}$ m). AFM software PicoScan5 was used to calculate root-mean-square roughness (Rq) and arithmetic mean roughness.

Interlaminar shear strength (ILSS) of fiber/PPESK composites was tested according to ASTM D2344 standard using three-point short-beam bending on an RG 3050 universal testing machine. Test conditions were 20°C and 50% relative humidity. Specimen dimensions were 25 mm × 6 mm × 2 mm with a span-to-thickness ratio of 5:1. Crosshead loading rate was 2 mm/min, with average values taken from five specimens per group.

Single fiber tensile strength (SFTS) was measured using an INSTRON 5567A universal materials testing machine to evaluate changes in fiber tensile properties after plasma modification. Following ASTM D3379-75 standard, individual fiber filaments were securely fixed on paper frames with adhesive. Testing was conducted at room temperature using a 100 N load cell, with a gauge length of 25 mm and tensile rate of 1.0 mm/min. Average values were obtained from multiple specimens per group.

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3. Results and Discussion

3.1 Changes in Surface Element Content

Variations in atmospheric air DBD plasma process parameters affect the surface chemical properties of PBO, Armos, and Twaron continuous fibers [18-20]. For example, with constant treatment time (10 s), the oxygen content on PBO fiber surfaces initially increases then decreases with increasing discharge power, reaching a maximum at approximately 225 W, while nitrogen content also shows significant improvement. Under constant discharge power, the surface oxygen and nitrogen content of Armos and Twaron fibers exhibit distinct variation patterns with increasing treatment time. This study selected moderate discharge power and treatment time parameters to modify the three fiber types and comparatively analyzed their surface chemical property changes under identical treatment conditions.

[Figure 2: see original paper] shows the changes in surface oxygen and nitrogen content of PBO, Armos, and Twaron continuous fibers before and after atmospheric air DBD plasma treatment at 150 W for 10 s, with growth rate comparisons presented in [Figure 3: see original paper]. As shown in [Figure 2: see original paper], the oxygen content on all three fiber surfaces increased significantly after plasma treatment under identical conditions, with nitrogen content also showing an upward trend. However, [Figure 3: see original paper] reveals clear differences in the growth rates of surface oxygen and nitrogen content among the three fibers: PBO fiber exhibited the highest growth rates at 55.6% for oxygen and 93.8% for nitrogen; Armos fiber showed intermediate values of 51.4% and 32.8%, respectively; while Twaron fiber displayed the lowest increases at 24.3% and 1.4%, respectively. The difference in nitrogen content growth was particularly pronounced.

The energy of active particles in plasma is typically several to tens of electron volts, while common chemical bonds in polymers have bond energies of 4.3 eV for C–H, 3.4 eV for C–C, 2.9 eV for C–N, 6.1 eV for C=C, and 8.0 eV for C=O [21]. Under the influence of plasma active particles, molecular bonds on polymer surfaces break, enabling combination with radicals generated in the discharge space to introduce new elements and functional groups [22, 23]. As shown by the chemical structures in , PBO fiber structural units contain a benzodioxazole heterocycle with two nitrogen atoms, while Armos fiber units contain a benzimidazole heterocycle with one nitrogen atom. Under bombardment by electrons, metastable particles, and high-energy radiation in plasma, nitrogen atoms in the heterocyclic structures within the top few molecular layers appear more susceptible to bond cleavage [24], forming nitrogen-containing fragments that enter the plasma. These then combine with active radicals containing nitrogen and oxygen formed through plasma oxidation, attaching to active sites on the outermost molecular layer and increasing surface nitrogen content while also contributing to oxygen content growth. Twaron fiber molecules lack such heterocyclic structures, so the process involves only the introduction of oxygen-containing radicals from the discharge space onto the fiber surface, resulting in increased oxygen content while nitrogen content remains essentially unchanged. Thus, the molecular composition of the fibers influences the effectiveness of plasma modification on surface chemical composition.

3.2 Changes in Surface Physical Morphology

Atmospheric air DBD plasma contains various active particles and high-energy radiation (such as UV light), and its action on fiber surfaces is essentially an energy transfer process. In addition to increasing oxygen and nitrogen content through combination with radicals from the discharge space, treated fiber surfaces undergo degradation and crosslinking reactions that produce surface roughening [22]. Previous studies have addressed the effects of atmospheric air DBD plasma parameter variations on the surface physical properties of the three fiber types [18-20], revealing consistent trends: surface roughness increases with discharge power at constant treatment time, and increases with treatment time at constant power; excessive discharge power or treatment time causes varying degrees of surface damage. Building on this foundation, this study selected moderate parameters of 150 W and 10 s to modify the three fiber types and further compared their surface physical morphology changes under identical treatment conditions.

[Figure 4: see original paper] presents SEM images showing surface morphology changes of PBO, Armos, and Twaron continuous fibers before and after atmospheric air DBD plasma treatment. Under equivalent plasma treatment, the three fibers exhibited different degrees of etching. Twaron fiber surfaces developed deep axial grooves and prominent protrusions, indicating substantial etching. Armos fiber surfaces showed slight deepening and widening of existing shallow groove features, with large-area etching traces appearing. PBO fiber surfaces only exhibited shallow axial groove structures [18] with relatively mild etching. lists the surface roughness changes of the three fibers before and after DBD plasma treatment, consistent with SEM observations. Notably, the degree of surface etching (PBO $<$ Armos $<$ Twaron) showed an inverse relationship to the magnitude of oxygen and nitrogen content increase (PBO > Armos > Twaron), indicating that chemical structure changes and physical morphology changes on fiber surfaces under plasma treatment are not directly correlated.

These results may be related to the inherent thermal stability of the fibers. Atmospheric air DBD plasma is a low-temperature plasma, also known as non-equilibrium plasma. Although ions and molecules remain near room temperature (approximately 300–500 K), electron temperatures reach 10^4 K [25, 26], producing intense local etching or ablation effects that alter surface morphology. As shown in , among the three fibers selected in this study, PBO exhibits the best thermal stability, followed by Armos, with Twaron being relatively less thermally stable, which correlates with the observed etching degrees.

3.3 Effect of Plasma Treatment on Composite Interfacial Properties

[Figure 5: see original paper] illustrates the ILSS values and growth rate comparisons for PBO, Armos, and Twaron continuous fiber-reinforced thermoplastic PPESK resin matrix composites before and after DBD plasma modification. Based on the above results, atmospheric air DBD plasma treatment modifies fiber surface chemical composition and physical morphology, thereby improving surface properties through introduction of active functional groups and surface roughening [27]. After plasma treatment, Twaron fibers showed relatively small increases in surface oxygen and nitrogen content (24.3% and 1.4%, respectively) but the most pronounced etching (deep grooves and protrusions). The increased surface roughness and surface area enhanced resin wetting and mechanical anchoring, resulting in a substantial ILSS increase of 24.8% for Twaron/PPESK composites. Conversely, PBO fibers exhibited minimal etching (only shallow grooves) but the greatest introduction of oxygen and nitrogen elements (55.6% and 93.8%, respectively). The enhanced surface polarity and reactivity similarly promoted hydrogen bonding and chemical bonding with the resin matrix, yielding a significant ILSS increase of 18.6% for PBO/PPESK composites.

ILSS results demonstrate that interfacial bonding strength in fiber-reinforced composites is jointly influenced by fiber surface chemical composition and physical morphology. Combined XPS, SEM, and AFM analyses reveal that the amount of oxygen and nitrogen introduced affects the degree of surface polarization and the number of active sites, while surface roughness influences the available surface area and mechanical anchoring points. These are two critical factors determining the interfacial properties of fiber-reinforced resin matrix composites. Under the selected atmospheric air DBD plasma treatment conditions in this study, the oxygen/nitrogen increments (see [Figure 3: see original paper]) and roughness changes (see) of PBO, Armos, and Twaron fiber surfaces were affected to varying degrees, resulting in different levels of interfacial property improvement. Data analysis indicates that Twaron fibers, which exhibited greater physical morphology changes, produced composites with relatively larger ILSS improvements, suggesting that physical morphology changes play a relatively dominant role in enhancing interfacial bonding performance.

3.4 Effect of Plasma Treatment on Fiber Tensile Properties

Atmospheric air DBD plasma treatment can alter fiber surface chemical composition and physical morphology, improving wettability, compatibility, and interfacial adhesion through introduction of active groups and surface roughening. However, surface modification based on plasma technology may also negatively affect the bulk properties of fibers. Previous studies by the authors investigated the effects of atmospheric air DBD plasma modification on the tensile properties of PBO and Armos fibers [18, 19]: PBO fiber SFTS decreased with increasing discharge power at constant treatment time, while Armos fiber SFTS decreased with increasing treatment time at constant power.

[Figure 6: see original paper] shows the SFTS changes of PBO, Armos, and Twaron fibers before and after plasma treatment at 150 W for 10 s. The average SFTS of all three modified fibers decreased to varying degrees compared to untreated fibers, as active particles in air DBD plasma bombard the fiber surface and introduce defects (see [Figure 4: see original paper]) that create stress concentration points [28], damaging mechanical properties. However, the reduction in tensile properties for all three fibers remained below 2%, indicating insignificant effects. These SFTS results demonstrate that appropriate atmospheric air DBD plasma treatment conditions can improve surface chemical properties by increasing oxygen and nitrogen content and enhance physical properties by roughening fiber surfaces while essentially maintaining bulk fiber properties, confirming that atmospheric air DBD plasma is an effective surface modification technique for organic fibers.

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4. Conclusions

1. After identical air plasma modification, although the oxygen and nitrogen content on all three fiber surfaces increased significantly, the growth rates differed markedly, indicating that modification effectiveness is related to the chemical structure of the fiber surfaces.
2. Under equivalent plasma modification conditions, the three fiber types exhibited different degrees of surface etching that did not correlate with the magnitude of surface chemical composition changes, possibly related to the inherent thermal stability of the fibers.
3. Improved fiber surface properties enhance bonding with resin matrices, with interfacial adhesion of fiber-reinforced composites being jointly influenced by surface chemical composition and physical morphology. Under the atmospheric air DBD plasma treatment conditions selected in this study, changes in physical morphology played a relatively dominant role in improving interfacial bonding performance.
4. Active particles in atmospheric air DBD plasma bombard fiber surfaces and introduce defects, resulting in reduced average single fiber tensile

strength after modification. However, the tensile property reduction for all three fibers remained below 2%, indicating negligible effects.

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