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Effects of argon plasma treatment on the interfacial adhesion of PBO fiber/bismaleimide composite and aging behaviors

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ABSTRACT

This paper is concerned with the influence of argon plasma on the interfacial adhesion of PBO fiber/bismaleimide composites and aging behaviors. The interlaminar shear strength (ILSS) was greatly increased to 62.3 MPa with an increase of 39.7% after treatment for 7 min at 80 Pa, 200 W. A small amount of O and N atoms was incorporated onto the fiber surface, but the plasma caused C–O bonds to break and generated O=C–N groups. The fiber surface roughness increased, contributing much to the wettability. However, long-time treatment excessively destroyed the inherent and newly created structures. The SEM images suggested that the fracture shifted from the interface to the matrix. The modification effects degraded with storage time in the air and the ILSS decreased to approximately 54.0 MPa after 10–30 days. The composite had low water absorption of 2.0 wt% and a high retention of 90% in the ILSS at moisture conditions.

1. Introduction

In the 1980s, the U.S. Air Force developed a specific polymer with rigid-rod structure—poly(*p*-phenylene benzobisoxazole) or PBO. Fibers prepared from this polymer by Toyobo (Japan) have two types: as-spun (AS) and high-modulus (HM) version, in which the tensile strength, Young's modulus and decomposition temperature of the latter are 5.8 GPa, 280 GPa and 650 °C, respectively [1–4]. These properties are far superior to other polymeric fibers, such as nylon 66, Kevlar and Spectra, and make the fibers suitable reinforcements in advanced resin matrix composites employed in the aerospace and aeronautics fields. In addition to their remarkable mechanical and electrical properties, thermosetting bismaleimide (BMI) resins possess high heat deflection temperature of above 250 °C, which far surpasses the value of traditional epoxy resins [5–8]. Thus, PBO/BMI composites have great potential for applications as structural materials which demand weight reduction, high strength and elevated temperature resistance. However, interfacial adhesions of the PBO/BMI composites are weak because of the fibers' smooth and inert surface.

The mechanical performance of fiber-reinforced polymer composites primarily depends on the fiber tensile strength and the interfacial bonding characteristics between fiber and matrix [9]. The interlaminar fracture of composites is usually caused by delamination of the fiber/matrix plies, longitudinal rupture along the fiber orientation or debonding between fiber and matrix due to poor interfacial adhesion [10]. The interface plays an important role in transferring stress from the matrix to the fiber, so the control of interfacial bonding is vital to strengthening fiber-reinforced polymer composites.

Low-temperature plasma processing is established as an effective and environmentally friendly method to improve the interfacial properties by modifying the physical and chemical characteristics of the polymers surface layer without influencing their bulk mechanical properties [11,12]. In our former research, the reactive oxygen plasma was used to strengthen the PBO/BMI interfacial adhesion with a maximum increase of 28.9% in the interlaminar shear strength (ILSS) [13]. In this study, the non-reactive argon plasma was applied to improve the interfacial adhesion.

The interfacial adhesion mechanism and the influence of the argon plasma processing time on interlaminar shear strength of the composites were studied. The surface free energy of PBO fibers was evaluated by dynamic contact angle analysis (DCAA). Changes in the surface chemical composition and surface roughness of PBO fibers before and after treatment were analyzed by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM), respectively. The fracture mechanisms of composites were examined by scanning electron microscopy (SEM).

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2. Materials and experiment

2.1. Materials

PBO (HM, Toyobo Ltd., Japan) fibers were cleaned consecutively with acetone and distilled water for 24 h at room temperature to remove surface sizing. The fibers were then dried at 105 °C in a vacuum oven for 3 h before argon plasma treatment.

BMI resin, with viscosity in the range 0.5–1.5 Pa s at 80 °C, was received from AVIC Beijing Aeronautical Manufacturing Technology Research Institute.

2.2. Methods

Continuous PBO fibers were rolled on glass frames and then put into a vacuum chamber with a 1 kW radio frequency (13.56 MHz) energy source. Argon was fed into the chamber at a flow rate of 150 SCCM to keep the chamber pressure at 80 Pa. The fibers were treated for 3–20 min at 200 W.

PBO fibers were impregnated with the BMI/acetone (40 wt%) solution using a wet winding process. The impregnations were dried at 40 °C for 1 h in a vacuum oven to keep the volatile content below 2.5 wt%. The composite was prepared by compression molding successively at 130 °C for 1 h, 190 °C for 3 h, and 235 °C for 3 h.

The interfacial adhesive strength of the PBO/BMI composites was measured by the three-point, short-beam bending test method, conforming to JC/T 773-1996. Each ILSS value was the average of more than five successful measurements.

Composite humid resistance tests were carried out by measuring the rates of water absorption and retained mechanical performance. The composite specimens were boiled in distilled water and their weights were measured at a constant interval time. When the weight increase was less than 0.001 g, the specimens were taken out and tested immediately to obtain their retained values of the ILSS.

The surface free energy of PBO fibers was measured by a dynamic contact angle analysis system (DCA-322, Thermo). The surface chemical components of PBO fibers were examined by X-ray photoelectron spectroscopy (XPS) (ESCALAB 250, Thermo). The photoelectrons were excited using a Al Kα ($h\nu$ = 1486.6 eV) monochromatic X-ray source with a voltage of 15 kV. The pass energy and step energy were 50 eV and 0.1 eV, respectively. Spectra were acquired at a take-off angle of 45° relative to the fiber surface. The surface roughness and morphology of PBO fibers were analyzed by atomic force microscopy (AFM, Picoplus II, Agilent) in tapping mode. Interlaminar shear rupture morphologies of PBO fiber-reinforced BMI composites were observed by scanning electron microscopy (QUANTA 600, FEI).

3. Results and discussion

3.1. Influence of argon plasma processing time on the ILSS

The physical and chemical structures on the fiber surface are continually changed with the exposure time; some new structures are created replacing the inherent ones, so the treatment time greatly influences surface properties of the fibers and their adhesion with resins [12,14]. The suitable treatment time depends on the gas, facilities and fiber–matrix systems, as well as the plasma condition.

Fig. 1 shows the dependence of the ILSS on the argon plasma processing time. After 3 min of exposure, the interfacial adhesion had a remarkable increase. The ILSS reached a maximum value of 62.3 MPa with an increase of 39.7% when the fibers had been treated for 7 min. However, the ILSS decreased rapidly when the exposure time was 10 min and then slowly to about 57 MPa as the length of exposure reached 20 min. Thus, from the point of interfacial adhesion, the fiber surface experienced a degradation process when the treatment time was from 7 to 20 min. The long-time treatment might result in excessive changes on the fiber surface or loss of mechanical properties of the fibers. It was apparent that there existed an optimum processing condition.

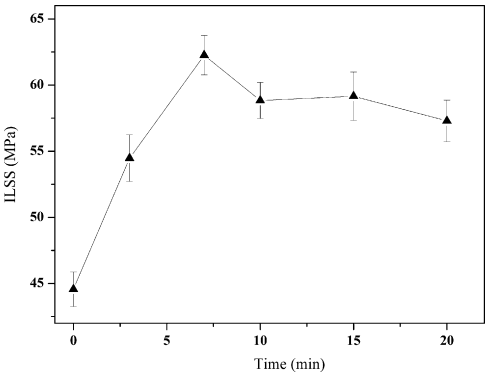

Fig. 1. Dependence of the ILSS on the processing time.

In comparison with our former research using oxygen plasma [13], the argon plasma treatment is more effective and time-saving. The analyses on the fiber surface can provide much information about different mechanisms of the strengthened interfacial adhesion.

3.2. Chemical composition of the fiber surface

The chemical composition of fiber surface dramatically affects the wettability and interfacial bonding between fiber and matrix [15]. The concentrations of elements can be determined by XPS. Table 1 lists the surface elements of the PBO fibers before and after treatment.

As shown in Table 1, the pristine fiber had a very high content of carbon atoms and relatively low concentrations of polar atoms, which contributed much to the inertness and poor wettability of the fiber surface. After treatment, the amount of carbon decreased and the O and N atomic percentage increased. The argon plasma consists of non-reactive particles in contrast to the oxygen and nitrogen plasma. Those particles transferred energies to the fiber surface and activated the surface layer by collisions, rather than combining with the fiber like the oxygen and nitrogen plasma [16], so the O and N increases were supposed to result from interactions with the residual air in the plasma reactor or from post-plasma reaction with the air after the treated fibers were taken out of the processing chamber [17,18].

The O/C atomic ratio increased from 0.25 to the highest value of 0.29 when the fibers were treated for 7 min. In comparison with our former research using oxygen plasma [13], the O/C increase was too small to significantly improve the wettability of the fiber surface. Additionally, the increase of N atoms could not exert much

Table 1
Surface elements of PBO fibers.

Time	Relative concentration of elements (at.%)			O/C	N/C
	C	O	N		
Untreated	75.4	18.7	5.9	0.25	0.08
3 min	70.0	20.5	9.5	0.29	0.14
7 min	70.5	20.4	9.1	0.29	0.13
15 min	73.1	19.6	7.3	0.27	0.10