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Effects of different fluorination routes on aramid fiber surface structures and interlaminar shear strength of its composites

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ABSTRACT

Poly-p-phenylene-benzimidazole-terephthalamide (PBIA) fiber was surface modified by direct fluorination under three different routes. The fiber was dried under vacuum to remove physisorbed water trapped on it and then fluorinated by the fluorine and oxygen gases or by the fluorine gas only. Results show that the interlaminar shear strength (ILSS) value of these two kinds of fluorinated fiber reinforced epoxy resin was 43.9 MPa and 51.0 MPa, which was improved about 14.0% and 32.5% compared with that of the virgin fiber (38.5 MPa), respectively. In the third route, the fiber was fluorinated by the fluorine and oxygen gases without removing physisorbed water, and the ILSS value decreased for nearly 31.2%, i.e. from 38.5 MPa to 26.5 MPa. X-ray photoelectron spectroscopy (XPS) showed that oxygen-containing and fluorine-containing chemical groups were introduced onto the fiber surface after fluorination, providing a stronger chemical bonding to polymeric matrices. Scanning electronic microscopy (SEM) indicated that the surface morphology of the fluorinated PBIA fiber varied with the different fluorination routes. A mass of compact micro groove structures was formed by the route that the fiber was dried to remove physisorbed water and then fluorinated with fluorine gas only. And these structures would markedly improve the ILSS of the composites. But, a mass of unstable flake surface structures was formed by the route that the fiber was fluorinated with the fluorine and oxygen gases without removing physisorbed water. And these structures would be the weak interface between the fiber and matrix and decrease the ILSS, even a lot of polar chemical groups were bonded onto the fiber surface as well.

1. Introduction

Para-aramid fibers, such as Armos, Kevlar, Twaron, and PBIA, have been widely used as reinforcement in the fields of space engineering, aviation and military application due to their high strength and modulus [1,2]. However, the inert chemical structure and smooth surface of the high performance aramid fibers, which prevent chemical bonding and mechanical interlock to polymeric matrices, directly lead to the weak interfacial adhesion between aramid fibers and polymeric matrices, thus restricting the application of the composites [3,4].

Previous publications by various authors have reported on extensive researches about the surface of aramid fibers and means to improve their interfacial adhesion between fibers and polymeric matrices. Also a variety of relatively efficient methods of surface modification have been proposed, such as chemical treatment [5,6], plasma treatment [7,8], γ-ray radiation treatment [9,10], ultrasound treatment [11], etc. However, some of their negative effects are fatal and unavoidable. For example, plasma activation is not durable in surface modification with time [7,12], and most of the upper methods above are applicable only to laboratory experiments but not to mass production.

Direct modification of polymer surface with the fluorine gas has been rapidly developed in recent years. Due to the gaseous diffusion and high reactivity of fluorine, direct fluorination technology can be applied for most of polymer materials regardless of the external and internal shape of the materials, so it is more suitable for industrial production [13–16]. At the same time, the thickness of the modified layer is about 0.01–10 μm range, which means the bulk properties of the polymer remain unchanged [17,18].

Nowadays, more and more researchers have paid attention to use this technology to resolve the problem of the interfacial adhesion between fibers and polymeric matrices. Mukherjee et al. [19] discussed about the fluorinated short Kevlar fiber reinforced composites, and reported that both the dispersion of Kevlar fibers and the interfacial adhesion were improved after fluorination. Peng et al. [20] investigated the surface modification of aramid fibers by direct fluorination, and the results indicated that the interfacial adhesion was markedly improved after direct fluorination. Both

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proposed that direct fluorination would improve the interfacial adhesion between fibers and polymeric matrices and were more inclined to attribute the cause of the improved interfacial adhesion to the polar chemical groups produced after fluorination. However, Solomun et al. [21] found that some amide bonds in aliphatic polyamide were decomposed during direct fluorination, also that decomposition of amide bond would also take place on aromatic polyamide during fluorination. That is to say, by inappropriate fluorination, amide bond in aramid fiber surface may decompose to form loose physical structure, which directly leads to worse interfacial adhesion, although lots of polar chemical groups are bonded onto the fiber surface. Therefore, it is worth of further study on the effects on the physical and chemical structure of the fiber surface under different fluorination routes.

In this study, three different fluorination routes were carried out to modify the surface of PBIA fiber. The results indicated that different fluorination routes would lead to different ILSS values of the fiber reinforced epoxy resin composites, and the fluorinated fiber could increase the ILSS value of its composites. In some cases, however, the ILSS value of the fluorinated fiber reinforced epoxy resin composite even appear to have significantly decreased compared with that of the virgin fiber reinforced epoxy resin composite Therefore, we studied the effects of different fluorination routes on PIBA fiber surface properties and the ILSS value of fluorinated PBIA fiber reinforced epoxy resin composite and analyzed the reasons of the increase and/or the decrease of the ILSS values by X-ray photoelectron spectroscopy (XPS), scanning electronic microscopy (SEM), respectively.

2. Experimental

2.1. Materials

The PBIA fibers (poly-p-phenylene-benzimidazole-terephthalamide) with a linear density of 150 tex were supplied by Sichuan Phaeton New Technology Co., Ltd. The F_2/N_2 (10 vol%) mixed gas was obtained from China Nuclear Honghua Specialty Gases Co., Ltd. The purity of mixed gas was more than 99.9%. Epoxy resin E-51 was supplied by Tianjinyanhai Chemical Co., Ltd. (Tianjin, China).

2.2. Direct fluorination treatment

The three different fluorination routes are described as following: Route one, the PBIA fiber was dried in the drying oven under vacuum at temperature of 120 °C for 5 h to remove physisorbed water (about 2 wt%) trapped on the fiber and then fluorinated in closed stainless steel vessels at temperature of 50 °C. Both of the fluorine gases and oxygen gases partial pressure in the fluorination ambience was 5 kPa. Route two, the PIBA fiber was dried before fluorination and then fluorinated with 5 kPa fluorine gas without oxygen gas. The drying condition of PBIA fiber and the fluorination temperature were the same as Route one. The only difference between Route one and Route two was that no oxygen gas existed in the fluorination ambience in Route two. Route three, the PBIA fiber was fluorinated with 5 kPa fluorine gas and 5 kPa oxygen gas at 50 °C without drying, which means that physisorbed water was still trapped on the fiber during fluorination. The PBIA fiber with these three different routes was orderly denoted as D-OF-PBIA, D-F-PBIA and UD-OF-PBIA.

2.3. Composite specimen preparation and characterization

PBIA fiber reinforced epoxy composites were prepared by the NOL-ring model. The Φ150 mm NOL-rings were twined over a 150 mm diameter steel mandrel. The curing system was made of epoxy resin E-51, maleic anhydride as curing agent, and N,N-dimethylbenzylamine as the accelerating agent, which was mixed at the ratio of 100:70:1 by weight, respectively. The thickness of the NOL-rings was about 2 mm and the content of the resin in composite was about 35 wt%. The curing process was shown as follows: 100 °C for 1 h, 120 °C for 2 h, and 150 °C for 2 h. Once the specimens were cured, which were needed to be cut into 6 mm width rings and the 6 mm width ring needed to be cut further into 20 mm lengths. The ILSS was tested on an Instron 4505 universal testing machine (USA) using a three-point short beam shear test method according to ASTM D 2344–2376. The specimens, whose dimensions were 20 mm × 6 mm × 2 mm, with a span to thickness ratio of 5, were tested at the rate of cross-head speed 2 mm min^{-1}.The ILSS (Γ) for the short beam test was calculated according to the following expression:

$$\Gamma = \frac{3P_b}{4bh}$$

where Γ is the interlaminar shear strength in MPa, P_b is the maximum compression load at fracture in Newton, b is the width of the specimen in mm, and h is the thickness of the specimen in mm. Each reported ILSS value was the average of more than eight successful measurements.

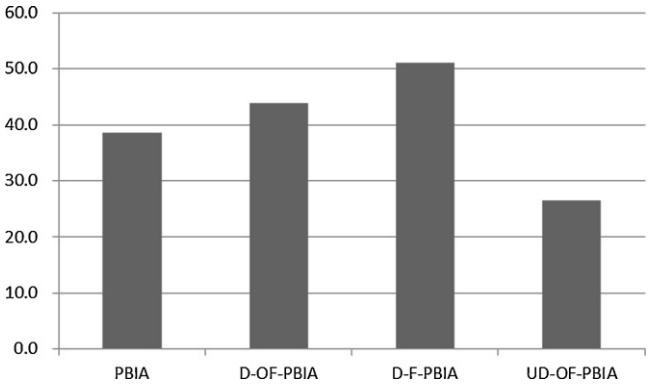

Fig. 1. ILSS of PBIA fibers and fluorinated PBIA fibers reinforced epoxy resin.

2.4. Characterization

XPS measurements were carried out on a Kratos ASAM 800 spectrometer (Kratos Analytical Ltd., U.K.), making use of non-monochromatic Al Kα (1486.6 eV) X-ray source (a voltage of 15 kV, a wattage of 250 W) radiation. The vacuum chamber pressure was controlled at a range of 10^{-6}–10^{-7} Pa. SEM (FEI Inspect F, FEI company, Europe) was operated with FEI Inspect F (FEI company, EU/USA) at 20 kV and the magnification was set at 10,000× and 80,000×.

3. Results and discussion

3.1. ILSS of the PBIA fiber reinforced epoxy resin composites

The ILSS results of fiber reinforced epoxy resin composites are shown in Fig. 1. The results were carried out by using ILSS tests of NOL-ring specimens of fiber reinforced epoxy resin composites. The ILSS value of the virgin fiber reinforced epoxy resin composites is 38.5 MPa, and that of D-OF-PBIA and D-F-PBIA increase to 43.9 MPa and 51.0 MPa, about 14.0% and 32.5% improvement compared with that of virgin one, respectively. However, the ILSS value of UD-OF-PBIA decreases by nearly 31.2%, from 38.5 MPa to 26.5 MPa.

The ILSS results indicate that the route that physisorbed water trapped on the PBIA fiber was removed before fluorination would