



Structural evolution of fluorinated aramid fibers with fluorination degree and dominant factor for its adhesion property



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ABSTRACT

Fluorination of aramid fibers using F_2 is a useful method to improve the adhesion property which is of great important for the mechanical performance of fibers-reinforced composites. In this paper, eight kinds of aramid fibers with different fluorination degree were prepared. With the increasing of fluorination degree, surface morphology and chemical structure of fibers both varied dramatically, such as appearance of $-C-F$ bond and $-COOH$ in the surface and the increased content, among which the variation of surface roughness and formation of $-C-F$ bond and $-COOH$ groups all contributed to the enhancement of pull-out strength of fluorinated aramid fibers from 0.43 to about 0.60 N/tex mm. Based on the contrast analysis, the appearance of chemical group $-COOH$ and increasing of its content are the dominant factor for the gradually improving the adhesion properties. Meanwhile, it was found that water soaking treatment after direct fluorination was a feasible method to further increase the $-COOH$ content and thus improve the pull-out strength to a higher level of 0.62 N/tex mm.

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1. Introduction

Aramid fibers such as Kevlar, Twaron and Armos are the high performance organic fibrous materials, which are widely used in commercial and industrial applications [1,2]. However, they offer a relatively inert surface, which limits potential chemical and mechanical interactions with polymeric resin systems and leads to the poor adhesion strength between fibers and epoxy resin [3–5]. The various conventional surface modification treatments are difficult to achieve high-effective activation and high-density functional group aggregation without damaging the surface structure [6–10]. Direct fluorination has been currently recognized as an effective method to modify and control physicochemical property of chemically inert polymers due to high reactive capability of fluorine gas [11–17]. The surface nature of activated layer can be controlled by direct fluorination introducing polar groups such as $-C-F$ bonds and some oxygen-containing groups regardless of whether polymers are hydrophobic or hydrophilic.

Peng et al. has reported that the direct fluorination of aramid fibers is a useful surface modification to improve the interlaminar shear strength (ILSS) of fibers/epoxy composites [13]. Further findings from Gao et al.'s study show that direct fluorination leads to the increasing of the surface polarity and roughness, and these chemical and physical changes play an important role in the improvement of interfacial adhesion property [18]. However, the above researches have not given a deep insight into the effect degree caused by each change of surface physical and chemical structure on the adhesion property of fibers. For example, direct fluorination would introduce $-COOH$, $-C-F$ groups, and induce a change of surface morphology, but each type may have a different contribution to the adhesion property. In order to optimize the adhesion property, it is necessary to identify the dominant factor to guide targeted treatment.

In the present work, we obtained the different chemical and physical structures of surface of aramid fibers (chemical structure in Fig. 1) by controlling the fluorination degree. The changing trends of surface structures of fluorinated aramid fibers are investigated. XPS and FTIR showed the transformation of categories and quantities of chemical groups in the process of direct fluorination. SEM and AFM indicated the varying of surface morphology and roughness with fluorination degree. It was found

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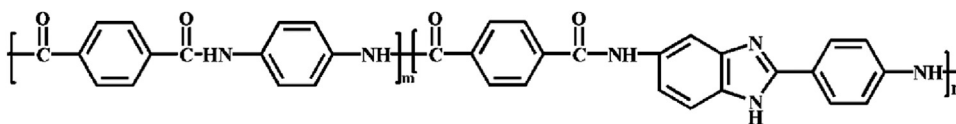


Fig. 1. the chemical structure of amide fiber.

that $-\text{COOH}$ content of surface was the dominant factor to improve the pull-out strength of fluorinated aramid in comparison with surface roughness and fluorine content in the surface. Therefore, introducing more $-\text{COOH}$ groups into surface could obtain a better adhesion property.

2. Experimental

2.1. Materials

The aramid fibers with a linear density of 100 *tex* were obtained from BLUESTAR Co., Ltd. The F_2/N_2 (10 vol% for F_2) mixed gas was supplied by Chengdu Kemeite Fluorine Industry Plastic Co., Ltd. Epoxy resin E-51 was obtained from BLUESTAR Co., Ltd. (Chengdu, China).

2.2. Surface modification

Direct fluorination of aramid fibers was carried out in sealed stainless steel chamber equipped with a vacuum line, and each sample has been treated together with aramid film. The air in the closed chamber was removed and replaced by nitrogen gas for three cycles to remove residual oxygen and moisture in the chamber. Different partial pressure of F_2/N_2 (vol%) mixture gas (0.2 kPa, 0.4 kPa, 0.8 kPa, 1.6 kPa, 6.4 kPa, 12.8 kPa, 25.6 kPa and 30 kPa) was introduced into chamber. After the completion of reaction, the gas in the chamber was pumped out, then N_2 gas (99.99% purity) was carefully introduced into the chamber until atmospheric pressure was reached, at which point the sample could be extracted. These fluorinated samples were orderly labeled as F-1, F-2, F-3, F-4, F-5, F-6, F-7, and F-8 in a sequence from low to high partial pressure of F_2/N_2 mixture gas for use. A part of F-4 sample was soaked in water immediately after direct fluorination for 24 h, then we got the fluorinated-water-soaking sample dried and labeled it as WF.

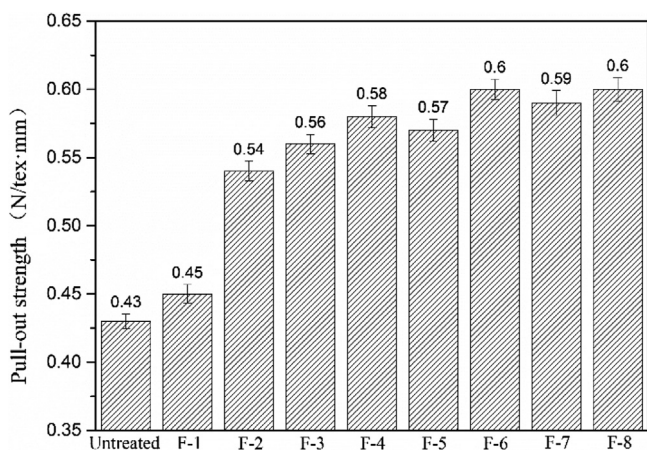


Fig. 2. The pull-out strength of fibers/epoxy composites with different fluorination degree.

2.3. Pull-out test preparation and characterization

The adhesion property of aramid fibers reinforced epoxy composites was characterized by pull-out test of specimen that was prepared by a bundle of fibers axially infiltrating in cylinder-shaped resin with thickness between 2 to 4 mm. The epoxy resin curing system was made of epoxy resin E-51 (BLUESTAR Co., Ltd), diamine (polyether amine with molecular weight of 230) as curing agent, which was mixed at the ratio of 3:1 by weight, respectively. The curing process was operated at ambient temperature for 48 h. The pull-out strength was tested on a universal testing machine (Instron 4505) using a tensile test method. The specimens were tested at the speed of 25 mm min^{-1} . The pull-out strength for the fibers-matrix was calculated according to the following equation (1):

$$\sigma = F/pd \quad (1)$$

where σ is the pull-out strength in $\text{N}/\text{tex mm}$, F is the debonding force for a given specimen in N , p is the linear density of a bundle fibers in *tex*, d is the embedded length mm. Every pull-out strength value was the average of more than ten successful measurements.

2.4. Characterization

The XPS data were collected on a Kratos ASAM 800 spectrometer (Kratos Analytical Ltd., U.K.) using a non-monochromatic $\text{Al K}\alpha$ (1486.6 eV) X-ray source (a voltage of 15 kV, a wattage of 250 W) radiation.

Nicolet 560 FTIR spectrometer (Thermo Electron) using Attenuated Total Reflection (ATR) mode was used to measure the changes in various functional groups on fiber surface. The spectra were measured in a wavenumber range of 4000–600 cm^{-1} .

SEM (FEI Inspect F, FEI Company, Europe) was carried out on a FEI Inspect F (FEI Company, EU/USA) at 20 kV and the magnification was set at 20,000 \times .

AFM (Picoplus, MI Ltd., U.S.A) images of observation were captured by tapping mode and operated under normal atmospheric pressure and temperature. The spring constant is 3 N/m, and the resonance frequency is 75 KHz. For the surface roughness values, each sample was tested for 5 times and the values were averaged

3. Results and discussion

3.1. Adhesion property of aramid fibers to epoxy

Adhesion property was tested by pull-out strength measurement. Fig. 2 shows the effect of direct fluorination on the pull-out strength of the fibers/epoxy composites. The pull-out strength was improved significantly after fluorination in comparison with that of the untreated fibers and increased gradually from 0.43 to about 0.59 $\text{N}/\text{tex mm}$ with fluorination degree. For samples from F-4 to F-8, the pull-out strength fluctuates between 0.57 and 0.60 $\text{N}/\text{tex mm}$, while the adhesion property was improved about 39% improvement by compared to the untreated one.

The enhancement of pull-out strength indicates the improvement of adhesion property may be contributed to the change of surface physical and chemical structures due to the direct

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