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Improved interfacial adhesion in carbon fiber/polyether sulfone composites through an organic solvent-free polyamic acid sizing

Haojie Yuan[a,b], Shouchun Zhang[a,*], Chunxiang Lu[a,*], Shuqing He[a,b], Feng An[a]

[a] National Engineering Laboratory for carbon fiber technology, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

An organic solvent-free polyamic acid (PAA) nanoemulsion was obtained by direct ionization of the solid PAA in deionized water, with the average particle size of 261 nm and Zeta potential of −55.1 mV, and used as a carbon fiber sizing to improve the interfacial adhesion between the carbon fiber and polyether sulfone (PES). The surface characteristics of PAA coated carbon fibers were investigated using Fourier transform infrared spectroscopy, scanning electron microscopy, atomic force microscopy and dynamic contact angle measurement. The results demonstrated that a continuous and uniform PAA sizing layer was formed on the surface of carbon fibers, and the surface energy of carbon fibers increased from 42.91 to 54.55 mN/m after sizing treatment. The single fiber pull-out testing was also performed, which showed the increased interfacial shear strength (IFSS) of carbon fiber/PES composites from 33.6 to 49.7 MPa by 47.9%. The major reasons for the improved interfacial adhesion were the increased van der Waals forces between the PES matrix and sizing layer as well as the chemical bonding between the sizing layer and carbon fiber surface. Furthermore, the PAA sizing also presented a positive effect on the interfacial adhesion of carbon fiber/PES composites under hydrothermal condition.

1. Introduction

With the increasing demand for the high strength and high fracture toughness composites in aerospace, automobile and other structural applications, great efforts have been devoted to the development of carbon fiber reinforced thermoplastic composites [1–7]. Among these, the carbon fiber/polyether sulfone (PES) composites have attracted wide attention [8–11] due to the superior properties of amorphous PES resins, such as high glass transition temperature (~225 °C), outstanding flame resistance and dimensional stability.

For a given reinforcement and matrix, the resulting mechanical properties of composites mainly depend on the interfacial adhesion [12], because the interface plays a critical role in stress transfer between the fiber and surrounding resin matrix. However, the chemically inert surface of carbon fibers seriously affects the interfacial adhesion in carbon fiber/PES composites. In recent years, a range of special surface modification methods have been applied to increase the interfacial adhesion between carbon fibers and thermoplastic resins, such as electrochemical treatment [13], plasma etching [8,14,15], high energy irradiation [16], grafting [17], and sizing treatment [18–21]. As for the sizing treatment, it can also protect carbon fibers from mechanical damage during subsequent textile processing and improve the wetting of carbon fibers by the resin matrices. Thus, the sizing treatment is an appropriate approach for tailoring fiber-matrix interface. Yumitori et al. [20] investigated the effect of a thermoplastic sizing consisting of amino-terminated PES on the interfacial adhesion of carbon fiber/PES composites. Chuang et al. [21] applied a polyamic acid (PAA) sizing to carbon fibers with PES matrix, and the increased interfacial strength was obtained. However, both the kinds of sizing agents contained strongly polar organic solvents. These organic solvents are difficult to remove from the fiber surface, and organic solvent vapors are harmful to the work environment. In view of the practical aspect, the sizing should be environmentally friendly and non-toxic. Therefore, it is technically important to develop an organic solvent-free thermoplastic sizing for the improvement of the interfacial adhesion between the carbon fiber and PES matrix.

In this work, we prepared an organic solvent-free PAA sizing by direct ionization of the PAA resin, and the PAA sizing was employed to increase the interfacial strength in carbon fiber/PES composites. The organic solvent-free sizing exhibits many advantages, such as facile preparation process, high storage stability and excellent compatibility with the current carbon fiber manufacturing processes, indicating the immerse potential for the industrial applications. In addition, the effects of the PAA sizing on the surface properties of

* Corresponding author at: 27 South Taoyuan Road, Taiyuan, Shanxi, China. Tel.: +86 351 4166215; fax: +86 351 4166215.
E-mail addresses: zschun@sxicc.ac.cn (S. Zhang), chunxl@sxicc.ac.cn (C. Lu).

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Table 1
Detailed properties of polyacrylonitrile-based carbon fibers used in this study.

Fiber type	Tensile strength (GPa)	Tensile modulus (GPa)	Failure strain (%)	Diameter (μm)	Density (g/cm^3)
MH300-3k	3.90 ± 0.10	230 ± 2	≥1.5	7.0 ± 0.1	1.76 ± 0.01

carbon fibers and the mechanism of interfacial adhesion between the carbon fiber and PES were also systematically investigated.

2. Experimental

2.1. Materials

The unsized polyacrylonitrile-based carbon fibers used in this study were supplied by the Institute of Coal Chemistry, Chinese Academy of Sciences, and the detailed properties are listed in Table 1. PES granules, E2010, were produced by BASF (Germany). 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA, 99% purity), 4,4′-oxydianiline (ODA, 98% purity), triethylamine (TEA, 99% purity) and N,N-dimethylformamide (DMF, 99.5% purity) were purchased from Shanghai Civi Chemical Technology Co., Ltd. (China) and used as received.

2.2. Preparation of PAA sizing and sizing treatment

In a typical synthesis procedure, the PAA resin was first synthesized from the equivalent molar ratio of BTDA and ODA in DMF at 15 °C under nitrogen. The resulting PAA solution was dried in a vacuum oven at 60 °C to remove the organic solvent and obtain the solid PAA resin. Next, TEA was added into the deionized water in a 1.05:1 molar ratio to carboxyl groups of PAA (two carboxyl groups per repeat unit) for complete ionization of the PAA resin. Then, 25 g of PAA resin was added into 100 ml of aqueous TEA solution with stirring for 30 min at 15 °C, and a ~20 wt.% PAA sizing was obtained. Finally, the as-prepared PAA sizing was diluted with 2.4 L of deionized water for a working concentration of ~1 wt.%. All above steps were further illustrated in Fig. 1.

Sizing treatment of carbon fibers was carried out by a conventional continuous process, as shown in Fig. 2. The fiber tows were first separated into individual fibers and then passed through the PAA sizing. Finally, the coated fibers were dried immediately in a hot gas oven at 100 °C, and the PAA sizing layer was obtained on the surface of carbon fibers.

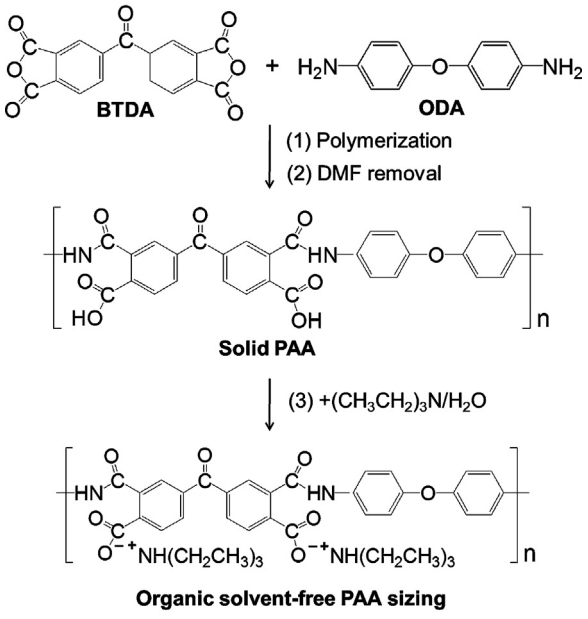

Fig. 1. Schematic diagram of the preparation of organic solvent-free PAA sizing.

2.3. Characterizations of PAA sizing and carbon fiber

The size distribution and Zeta potential of the PAA sizing were examined by a Zetasizer Nano particle analyzer (Zetasizer NANO ZS, Malvern, UK). The sample was tested as received and without further dilution. The morphology of colloidal particles was observed by TEM (Tecnai G2 F20, FEI, USA) at the magnification of ×10,000.

The surface functional groups of carbon fibers were analyzed using a FTIR spectrometer (Nicolet 8700, Thermo Scientific Instrument Co., USA) in attenuated total reflection mode. The FTIR spectra were obtained by scanning the samples for 32 times in the range of 2000–1000 cm^{-1} with the resolution of 2 cm^{-1}.

The surface morphologies of carbon fibers were observed by SEM (JSM-7001F, JEOL, Japan) at 10 kV. Prior to testing, the samples were coated with Au by sputtering. The values of the surface roughness (S_a) were evaluated by AFM (5500 AFM, Agilent Technologies, USA) in an area of 4 μm × 4 μm using tapping mode. The scanning frequency used was 1 Hz.

Dynamic contact angles were detected by a dynamic contact angle meter and tensiometer (DCAT21, Dataphysics Instruments, Germany). The surface energy (γ), polar component (γ^p) and dispersive component (γ^d) of carbon fibers were calculated through Owens-Wendt method [22]. Deionized water (γ = 72.8 mN/m, γ^p = 51.0 mN/m) and diiodomethane (γ = 50.8 mN/m, γ^p = 2.3 mN/m) were chosen as testing liquids.

2.4. Single fiber pull-out testing

The interfacial shear strength (IFSS) of carbon fiber/PES composites was examined by the single fiber pull-out testing on micro-droplet composites. A single fiber was fixed on a holder with adhesive tape, and a DMF solution of PES was spread on the single fiber to form micro-droplets due to the function of surface tension. The resulting sample was dried at 100 °C for 60 min in air, and then maintained at 300 °C for 30 min in nitrogen to make the PES resin fully wet the single fiber and convert the PAA sizing resin into PI resin. The maximum force to pull the single fiber out of the micro-droplet was measured on an interfacial strength evaluation instrument (MODEL HM410, Tohei Sanyon Co., Japan), and IFSS was calculated by Eq. (1) [23],

$$\tau_{IFSS} = \frac{F_{max}}{\pi d l} \quad (1)$$

where τ_{IFSS} is the value of IFSS, F_{max} is the maximum force, d is the carbon fiber diameter and l is the embedded length of carbon fiber

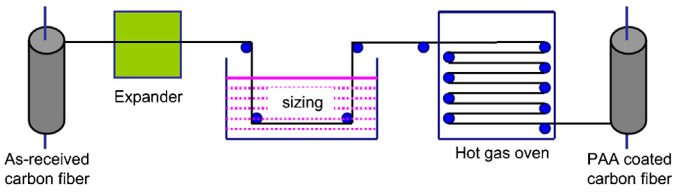

Fig. 2. Schematic diagram of the continuous sizing treatment of carbon fibers.

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