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RESEARCH PAPER

Preparation and characterization of a polyimide coating on the surface of carbon fibers

Hao-jie Yuan[1,2], Chun-xiang Lu[1], Shou-chun Zhang[1]*, Gang-ping Wu[1]

[1]National Engineering Laboratory for Carbon Fiber Technology, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China;

[2]University of Chinese Academy of Sciences, Beijing 100049, China

Abstract: Organic, solvent-free polyamic acid sizing was coated onto T300 grade carbon fibers (3k) to prepare a polyimide (PI) coating having a high thermal stability and oxidative resistance. The surface of PI-coated carbon fibers was characterized by FTIR and SEM. The mechanical strength of the carbon fibers, thermal stability and oxidative resistance of the coating were also investigated. Results indicate that a continuous and uniform PI coating is formed on the surface of the carbon fibers. Compared to a carbon fiber coating with epoxy, the PI coating produces excellent thermal stability with onset decomposition and a 5% weight-loss temperatures of 567 and 619 °C, respectively. The tensile strength of PI-coated carbon fibers after thermal oxidation in air at 400 °C for 1 h has only a slight decrease of 6%, which is significantly lower than the decrease of 22% for epoxy-coated fibers.

Key Words: Carbon fiber; Surface modification; Thermal stability; Polyimide coating

1 Introduction

Over the past few decades, carbon fibers have been the most attractive reinforcement for advanced composite materials[1-5]. Especially, with the advent of high temperature thermoplastics, structural applications for carbon fiber reinforced thermoplastic composites are increasing rapidly, owing to their high fracture roughness, excellent heat resistance, ease of manufacture and recyclability[6-8]. However, processing temperatures of these thermoplastics, such as polyether ether ketone, polyether sulfone and polyether imide, are generally higher than 300 °C, which is a critical challenge for the thermal stability of surface coatings on carbon fibers as sizing agents.

Commercial carbon fibers are commonly coated with a pure[9] or modified[10] epoxy coating to protect the fiber surface from the mechanical damage and improve the processability of fiber yarns. These coatings can hardly withstand high processing temperatures required for the high temperature thermoplastics, leading to a poor overall thermal stability of carbon fibers. Up till now, many anti-oxidative coatings had been fabricated onto carbon fibers, such as ceramic coatings[11-14], metal coatings[15-17] and multilayer coatings[18]. These coatings significantly increase the overall thermal stability of carbon fibers, but they are incompatible with thermoplastic matrices. The choice of a surface coatingslargely depends on the polymer matrix to obtain a strong interface bonding in a composite[19], and the high temperature thermoplastics require a thermal resistant polymer coating on the surface of carbon fibers. Aromatic polyimide (PI) is the most thermally stable polymer among commercial polymers[20], owing to its highly aromatic structure, and thus it is one of the best candidates for coating materials of carbon fibers used as reinforcement of high temperature thermoplastics. Cao et al.[21] applied a thermoplastic PI polymer to modify the epoxy coating to raise the thermal stability of surface coating on carbon fibers, but the existence of epoxy still restricted the level of thermal resistance. Naganuma et al.[22] directly obtained the PI coating on the surface of carbon fibers by a high temperature vapor deposition polymerization. Moreover, atomic layer deposition[23] is also a potential approach to prepare the PI coating onto carbon fibers. However, both two methods are very complex and incompatible with large scale manufacturing processes of carbon fibers. Sizing treatment is a common and effective approach to prepare the PI coating by a polyamic acid (PAA) sizing and thermal imidation, but the PAA sizings used in previous studies[24, 25] contain organic solvents. Organic solvent vapors are hazardous to the health of workers, and even lead to the explosive hazard.

In our previous study[7], we developed an organic solvent-free PAA sizing by direct ionization of the solid PAA in deionized water. In this work, we prepared the PI coating onto carbon fibers by sizing treatment with this organic solvent-free PAA sizing and thermal imidation. The facile preparation of the PI coating is compatible with large scale manufacturing processes, indicating the potential to transfer this technology into practice.

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***Corresponding author.** E-mail: zschun@sxicc.ac.cn

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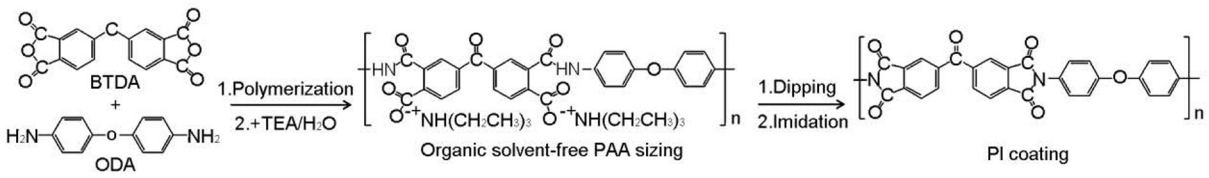

Fig. 1 Schematic diagram of the preparation of a PI coating onto carbon fibers from an organic solvent-free PAA sizing.

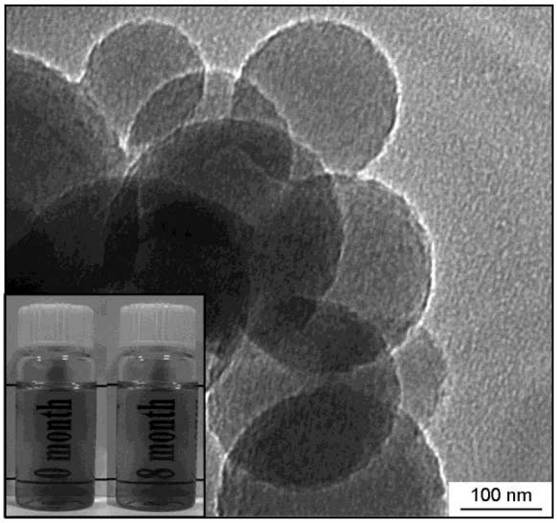

Fig. 2 TEM image of PAA colloidal particles and (inset) digital images of the PAA sizing after 0 and 8 month of standing.

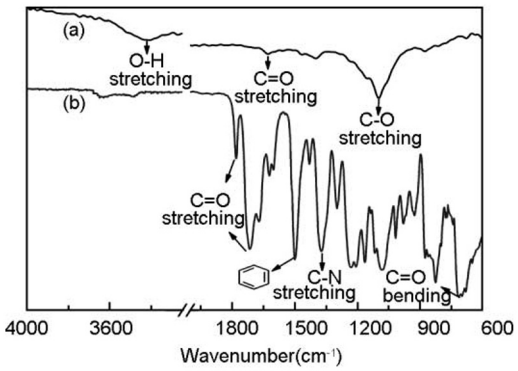

Fig. 3 FTIR-ATR spectra of (a) uncoated and (b) PI coated carbon fibers.

2 Experimental

2.1 Materials

Commercially available (with a conventional epoxy sizing) and unsized (labeled as uncoated) T300 grade carbon fibers (3 k) used in this study were produced by the Institute of Coal Chemistry, Chinese Academy of Sciences, and their specific physical properties were reported elsewhere[26]. 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), 4,4'-oxydianiline (ODA), N,N-dimethylformamide (DMF) and triethylamine (TEA) were purchased from Shanghai Civi Chemical Technology Co., Ltd. All the chemicals were of analytical reagent grade, and used without further purification.

2.2 Preparation of PI coating

In a 250 mL three-necked flask, 16.1 g (0.05 mol) of BTDA was added into 160 mL of DMF that dissolved in 10.0 g (0.05 mol) of ODA. After stirring under nitrogen for 2 h at 15 °C, a yellow-green PAA solution was obtained. The solution was heated in vacuum at 80 °C to remove DMF and obtain the solid PAA polymer. The weight-average molecular weight of PAA was 3.34×10^5 g/mol with a polydispersity index of 1.56 as determined by gel permeation chromatography (GPC). Meanwhile, 17 mL of TEA was added slowly into 2.6 L of deionized water to prepare an aqueous TEA solution. Finally, the organic solvent-free PAA sizing was obtained with a concentration of 1% by adding the solid PAA polymer into the aqueous TEA solution under stirring for 2 h at room temperature. Subsequently, uncoated carbon fibers were dipped into the above PAA sizing for 30 s and further heated at 100, 200 and 300 °C, each for 1 h in nitrogen. Then a PI coating was formed on the surface of carbon fibers from the organic solvent-free PAA sizing. The synthesis process is shown in Fig. 1.

2.3 Characterization

GPC was carried out on a Viscoteck GPC system using DMF with 20 mmol/L LiBr as a mobile phase. Transmission electron microscopy (TEM) was performed by a JEM-2010 electron microscope. Scanning electron microscopic (SEM) images were obtained using a JSM-7001F scanning electron microscope with an accelerating voltage of 9 kV. Infrared spectra were recorded using a Magna 750 Fourier transform infrared (FT-IR) spectrometer in attenuated total reflection (ATR) mode.

Thermogravimetric analysis (TGA) was performed on a SDT Q600 thermal analyzer with a heating rate of 10 °C/min in air. The temperature at which samples have lost 1% of their weight is defined as the onset decomposition temperature, T_d. The temperature at which 5% of sample lost weight is designated as T_5. Moreover, the isothermal aging of the samples was carried out using a muffle furnace at 400 °C in air for 1 h. After the aging treatment, the surface morphologies of specimens were observed by SEM and atomic force microscopy (AFM, Nanoscope 4) to further assess the thermal