Applied Surface Science 379 (2016) 199–205

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Effects of surface treating methods of high-strength carbon fibers on interfacial properties of epoxy resin matrix composite

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ARTICLE INFO

Article history:
Received 15 January 2016
Received in revised form 20 March 2016
Accepted 11 April 2016
Available online 13 April 2016

Keywords:
Carbon fiber
Epoxy
Electrolysis
Sizing agent
Surface treatment
Interfacial adhesion

ABSTRACT

This paper aims to study the effects of surface treating methods, including electrolysis of anodic oxidation, sizing and heat treatment at 200 °C, on physical and chemical properties of T700 grade high-strength carbon fiber GQ4522. The fiber surface roughness, surface energy and chemical properties were analyzed for different treated carbon fibers, using atom force microscopy, contact angle, Fourier transformed infrared and X-ray photoelectron spectroscopy, respectively. The results show that the adopted surface treating methods significantly affect surface roughness, surface energy and active chemical groups of the studied carbon fibers. Electrolysis and sizing can increase the roughness, surface energy and chemical groups on surface, while heat treatment leads to decreases in surface energy and chemical groups due to chemical reaction of sizing. Then, unidirectional epoxy 5228 matrix composite laminates were prepared using different treated GQ4522 fibers, and interlaminar shear strength and flexural property were measured. It is revealed that the composite using electrolysis and sizing-fiber has the strongest interfacial bonding strength, indicating the important roles of the two treating processes on interfacial adhesion. Moreover, the composite using heat-treating fiber has lower mechanical properties, which is attributed to the decrease of chemical bonding between fiber surface and matrix after high temperature treatment of fiber.

1. Introduction

The use of carbon fiber reinforced polymer matrix composites has substantially increased in the fields of aerospace, transportation, and sports goods due to their excellent properties, such as high specific strength, high specific modulus, and the ability to be tailored for specific applications[1–3]. At the same time, a great deal of scientific efforts have been focused on the analysis and the improvements in interfacial properties since it is well recognized that the interphase significantly impacts the final behavior of composites[4–6]. Interfacial adhesion is crucial and interfacial adhesion strength can, in general, be dominated by chemical bonding, mechanical interlocking (e.g. fiber surface roughness), physicochemical compatibility (e.g. polarity of the surface energy), and intricate combination of these factors[7,8].

Since the surface of pristine carbon fiber is non-polar and compound of highly crystallized graphitic basal planes with inert structures [9,10], the interfacial bonding strength between carbon fibers and polar resin matrix is low, and ideal mechanical properties of composites can not be necessarily achieved [11]. Thus, numerous methods concerning surface treatments on carbon fibers have been proposed to increase the surface functional groups and thus enhance the interactions and/or adhesion between carbon fibers and matrix [9,10,12]. Moreover, during manufacture process, commercial carbon fibers are always coated with a thin film of sizing agent after surface chemical treatment, such as electrolytic oxidation, acid washing and plasma treatment. The sizing agent usually presents as solution or emulsion consisting of polymeric components and assistants [11,13–17]. Surface chemical treatment can increase active functional groups on fiber surface, and sizing process mainly aims to protect fibers from damage, improve the handleability of fibers and increase the compatibility between fiber and matrix [18,19].

Sizing agent can change carbon fiber surface properties, as well as the wettability and chemical reactions with epoxy matrices [20–22]. Numerous studies also proved that sizing agent can significantly impact the interfacial adhesion between carbon fiber and resin matrix [21–24]. In addition, various surface chemical treatment techniques of carbon fiber have been studied, showing enhancement of interfacial adhesion between fiber and matrix

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http://dx.doi.org/10.1016/j.apsusc.2016.04.075
0169-4332/

Table 1
Surface treating conditions of GQ4522 carbon fiber.

Sample number	Treatment
1	electrolysis and sizing
2	electrolysis, sizing and heat treatment at 200 °C for 2 h in oven
3	electrolysis without sizing
4	sizing without electrolysis

resin [25–29]. However, there are few published papers simultaneously focusing on the effects of sizing and surface chemical treatment on surface property of carbon fiber and its interfacial adhesion with matrix. Considering irreversible interaction between sizing and active functional groups on surface of carbon fiber, understanding the roles of sizing and surface chemical treatment of carbon fiber on interfacial adhesion is necessary. In addition, before carbon fibers are used to fabricate composite, carbon fibers are often treated under high temperature for drying or processing requirement. This process might change the surface state of carbon fiber, and the effect on interfacial bonding should be clarified.

The objective of this study is to elucidate the influences of surface treatment on the interfacial properties between a kind of T700 grade high-strength carbon fiber with high-temperature cured epoxy (EP) resin. Firstly, carbon fibers were produced with different surface treating methods, including anodic oxidation, sizing and high temperature (200 °C) treatment. Then, advancing contact angle, atomic force microscope (AFM), Fourier transformed infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) were employed to analyze the surface physical and chemical properties of various carbon fibers. Furthermore, unidirectional carbon fiber composite laminates were produced by means of prepreg/autoclave process using different treated fibers. Finally, interlaminar shear strength (ILSS) and flexural property of the laminates were tested for evaluating the effects of surface treatment method of carbon fiber on the interfacial property of fiber/EP resin. Combined with the observation on fracture morphology, these results clearly demonstrate the important roles of each stage of surface treatment processing in interfacial adhesion of carbon fiber/EP.

2. Experimental

2.1. Materials

EP resin matrix, named 5228 was used for the matrix of composite in this paper. 5228 is a commercial available toughened EP resin supplied by Beijing Institute of Aeronautic Materials (BIAM), China. The standard curing cycle is recommended as 130 °C 1 h + 180 °C 2 h + 200 °C 2 h.

A kind of commercial T700 grade high-strength carbon fiber, named GQ4522 was used in this study, supplied by Weihai Tuozhan Fiber Co., Ltd. GQ4522 is fabricated by wet-spray wet-spinning process from PAN precursors, with 12 K filaments in a bundle, exhibiting tensile strength of 5221 MPa, tensile modulus of 254 GPa, elongation of 1.94%, volume density of 1.79 g/cm^3 and linear density of 803 g/km. Four kinds of GQ4522 fiber surface treating processes were carried out for obtaining carbon fibers with different surface properties. The conditions of surface treatment are listed in Table 1. Sample 1 has standard surface treating technique, which firstly electrolyses carbon fibers to a certain extent of anodic oxidation and then coats them with sizing. During anodic oxidation, NH_4HCO_3 solution was used for electrolyte, while graphite plate and carbon fiber respectively were cathode and anode. The temperature of electrolysis was 35 °C and the treating time was 85 s with 0.23 mA/cm^2 current density. The content of sizing was 1.5 wt.%. This kind of carbon fiber is usually used in industry application. Sample 2 was obtained from sample 1 after being heat treated at 200 °C for 2 h in an oven. This treatment was referred to the condition adopted by our study for T800 grade carbon fiber [19]. Our previous works had demonstrated that interfacial property of carbon fiber composite was significantly influenced by high temperature, which was ascribed to the effects of temperature on chemical reaction and diffusion between sizing and matrix resin [30,31]. Sample 3 is similar with sample 1, but it did not be coated sizing agent. In addition, sample 4 was treated using sizing without electrolysis process.

Unidirectional composite laminates of 5228/GQ4522 with the four kinds of surface treating methods were provided by BIAM. The laminates were produced using prepreg/autoclave process, and they had 2 mm thickness with 60% fiber volume fraction and less than 2% porosity. The cure process involves two steps, including cure process in autoclave and subsequent post-cure in oven. The cure cycle of autoclave process is as follows: 1 h 130 °C dwell with 0.6 MPa applied pressure and 2 h 180 °C dwell with maintaining pressure. The heating rate was 2 °C/min, and furnace cooling was carried out. The laminates were further cured in an oven under 200 °C for 2 h, which heating rate was 1 °C/min.

2.2. Characterization

2.2.1. Surface roughness of carbon fiber

Roughness of fiber surface was investigated by AFM (Dimension icon, Veeco) with a scanning region of 3 μm × 3 μm. Value of roughness (Ra) was obtained by NanoScope Analysis software and at least 25 valid data were taken for each sample.

2.2.2. Surface energy of carbon fiber

Advancing contact angles between reference liquid (water, formamide and diiodomethane) and single fibers were measured using a dynamic contact angle and surface/interfacial tension instrument (DCAT21, Dataphysics), according to modified Wilhelmy method. All of the contact angles were obtained at an immersion speed of 0.01 mm/s, with surface detection threshold of 0.15 mg and immersion depth of 3 mm at 25 °C. The experiment was carried out with five monofilaments tested at the same time, and each test was repeated three times. From the average contact angles and surface tension of the three kinds of reference liquid, surface energy of carbon fiber was calculated based on OWRK(Owens,Wendt, Rabel and Kaelble)method [32].

2.2.3. Chemical properties of carbon fiber surface

Chemical compositions of fiber surface were determined by XPS (ESCALAB 250, ThermoFisher Scientific), with a monochromatic Al Kα X-ray source and 500 μm spot size. 200 eV of pass energy for survey scan and 30 eV for high resolution scan were employed in all the measurements. A five-parameter curve fitting for the C1s spectra was conducted by taking 284.8 eV as the reference peak, and carbon atoms bonded with O were defined as activated carbon atoms. The proportion of activated carbon atoms was calculated by the sub-peak integral area ratio [19,33].

2.2.4. Reactivity of sizing agent

The surface sizing of carbon fiber was extracted by acetone using soxhlet extraction at 80 °C for 24 h. Then, the reactivity of extracted sizing agent was evaluated by FTIR spectroscopy (Nicolet 560). The spectra were obtained in an optical range of 400–4000 cm^{-1}. The changes of functional groups in sizing before and after heat treated at 200 °C were used to reflect its reactivity, in order to study the chemical change on fiber surface of sample 2 denoted in Table 1.