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Interface property of carbon fibers/epoxy resin composite improved by hydrogen peroxide in supercritical water

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ABSTRACT

Carbon fibers were treated by hydrogen peroxide in supercritical water and the surface morphologies of treated carbon fibers were observed by atomic force microscopy. It was found that surface roughness of the treated carbon fiber was improved obviously. Furthermore, X-ray photoelectron spectroscopy (XPS) was used to analyze surface functional groups of carbon fibers. It was found that functional groups containing oxygen were significantly increased compared with untreated carbon fibers. The maximal interlaminar shear strength (ILSS) of treated carbon fibers/epoxy resin composite was 110.5 MPa, which was higher than 63.5 MPa for untreated carbon fibers/epoxy resin composite. It also indicated that interface property of carbon fibers/epoxy resin composite was improved by hydrogen peroxide in supercritical water.

1. Introduction

Since the first commercial production of carbon fibers in the late 1960s, carbon fibers have been widely used as reinforcement materials in advanced composites because of their relatively low cost and excellent properties, such as high specific strength, stiffness, low expansion coefficient and relative flexibility [1,2]. However, when applied without previous surface modification, the physicochemical interaction between carbon fibers and its reinforced matrix is not tough enough due to the inert surface properties of carbon fibers, which will directly affect interfacial adhesion in the composites [2]. Surface oxidation of carbon fibers is commonly used to improve the adhesion between fibers and matrix in composites [3]. Numerous methods concerning surface treatment, such as chemical method, electrochemical method [4], plasma treatment [5], etc., have been developed to increase the quantity of surface functional groups and thus enhance the interactions between fibers and matrix. Furthermore, a supercritical fluid can be defined as a substance above its critical temperature and pressure. Under this condition the fluid has unique properties, in that it does not condense or evaporate to form a liquid or a gas [6]. In the past decade, supercritical fluids have been used in many different applications ranging from classical extraction to sophisticated industrial processes [7]. Nevertheless, there were few reports about carbon fibers treated by the supercritical fluids, especially by hydrogen peroxide in supercritical water.

In this paper, in order to increase the quantity of surface functional groups, carbon fibers were treated by hydrogen peroxide (3 vol.%) in supercritical water. The surface characteristic and morphologies of carbon fibers were investigated by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Furthermore, interface property between fibers and matrix in composites was evaluated by interlaminar shear strength (ILSS) of the composite.

2. Experimental

Commercially T-300™ carbon fibers with a diameter of about 6–7 μm were purchased from Japan Toray. E-51 epoxy resin was obtained from Yueyang Chemical Co. Ltd., China. Carbon fibers were treated in hydrogen peroxide (3 vol.%) in supercritical water for some time. The pressure of water was controlled beyond its critical point (374 °C, 22.1 MPa) by adjusting the volume of water in reactor at temperature of 450 °C. The phthalic anhydride was chosen as curing agent. Epoxy resin/phthalic anhydride/benzyl dimethylamine were 100, 70 and 1 parts by weight, respectively. The prepreg that was fabricated by treated carbon fibers and epoxy resin was put unidirectional into a mold to manufacture composites. The prepreg was pressed and cured under 5 MPa pressure for 2 h at 90 °C, then under 10 MPa pressure for 2 h at 120 °C and last under 10 MPa pressure for 4 h at 150 °C by hot-press machine and hot-pressed composite with fibers mass fraction of 65(±1.5%) and fibers volume fraction of 58(±1%). ILSS of the composites was measured by short beam bending test according to ASTM D-2344 using an Instron 1125. A span to depth ratio of 5:1, cross-head speed of 2 mm min^{-1}, and specimen thickness of 2 mm were used. The fracture morphology of the composite was observed using Hitachi S-4700 scanning electron microscopy (SEM). Carbon fibers were examined on a Russian solver P47 AFM. The XPS

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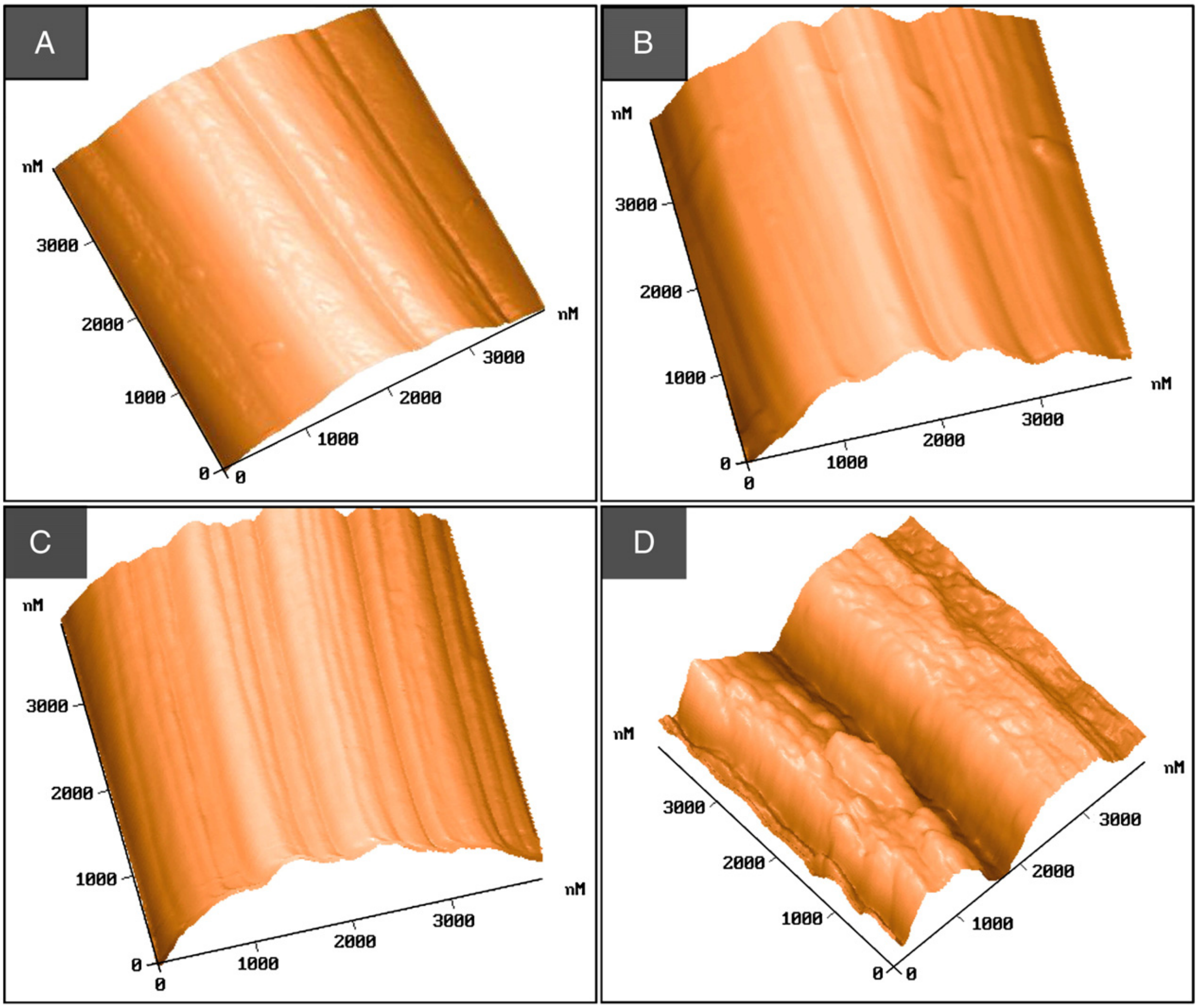

Fig. 1. The micrographs of treated carbon fibers surface for different treatment times. A, untreated; B, 10 min; C, 20 min; D, 30 min.

measurement of fiber surface was performed with an X-ray photoelectron spectrometer (Perkin-Elmer, PHI 5300).

3. Results and discussion

The surface of as-received carbon fibers is quite smooth as shown in Fig. 1(A). The surface of treated carbon fibers was changed by hydrogen peroxide in supercritical water with the treatment time increasing and many grooves appeared on the surface of carbon fibers as shown in Fig. 1(B)–(D). The surface roughness of carbon fibers was increased obviously with increasing treatment time. Moreover, many grooves on the surface of carbon fibers were incorporated into a deep furrow when the treatment time was more than 20 min.

The surface atomic compositions obtained by XPS analysis were summarized in Table 1. From these data, it was revealed that the surface of carbon fibers was mainly composed of carbon, oxygen and nitrogen. The carbon and oxygen contents of the untreated carbon fibers were 89.57 and 9.25% and the O/C ratio was 0.1033. The O/C ratio of treated carbon fiber as high as 0.3586 was significantly increased compared with the untreated fiber due to the surface oxidation of carbon fibers.

Table 1
XPS element contents of untreated and treated carbon fibers for 30 min.

Carbon fiber	Element content (%)			O/C
	C	O	N	
Untreated	89.57	9.25	1.18	0.1033
Treated	72.69	26.07	1.23	0.3586

XPS was used to further analyze the functional groups on the carbon fiber surface and the peaks of the detailed functional groups were presented in Fig. 2. In order to obtain the best fit between the experimental and the synthesized spectrum, a computer simulation estimated the intensity contribution of each functional component peak. Typical XPS spectrum of the C 1s peak region at 284.6 eV deconvoluted into surface functional group contributions were shown in Fig. 2A and B for untreated and treated carbon fibers, respectively. It was found that the C 1s peaks could be fitted to line shapes with binding energies at 284.6, 285.4 286.2 and 287.6 eV [1]. As a result, the total area of the C 1s peak region of untreated carbon fibers consisted of 58.48% C–C, 18.05% C–O, 16.99% C=O, 6.43% COOH. The total area of the C 1s peak region of treated carbon fibers consisted of 52.36% C–C, 2.73% C–O, 37.33% C=O, 7.56% COOH. These data were summarized in Table 2. Compared with untreated carbon fiber, the contents of C=O, COOH and CO_3^{2-} functional groups on the surface of carbon fibers was increased, however, the content of functional groups C–OH was decreased from 18.05% to 2.73%, which revealed that the surface of carbon fiber was oxidized. From these results, it could be detected that the contents of functional groups containing oxygen were significantly