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Plasma-grafting polymerization on carbon fibers and its effect on their composite properties

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ABSTRACT

Interfacial adhesion between matrix and fibers plays a crucial role in controlling the performance of composites. Carbon fibers have the major constraint of chemical interness and hence have limited adhesion with the matrix. Surface treatment of fibers is the best solution to this problem. In this work, carbon fibers were activated by plasma and grafting polymerization. The grafting ratio of polymerization was obtained by acid–base titration. The chemical and physical changes induced by the treatments on carbon fiber surface was examined using contact angle measurements, X-ray photoelectron spectroscopy (XPS), and Fourier-transform infrared spectroscopy-attenuated total reflectance (FTIR–ATR) technique. The interfacial adhesion of CF/EP (carbon fiber/epoxy) composites were analyzed by a single fiber composite (SFC) for filament fragmentation test. Experimental results show that the grafting rate was not only the function of the plasma-treat time but also the concentration of the grafting polymerization. The oxygen-containing groups (such as C—O, C═O, and O—C═O) and the interfacial shear strength (IFSS) of the plasma-grafting carbon fiber increased more significantly than the carbon fiber without plasma treatment grafted with MAH. This demonstrates that the surfaces of the carbon fiber samples are more active, hydrophilic, and rough after plasma-grafting treatments using a DBD operating in ambient argon mixture with oxygen. With DBD (dielectric barrier discharges) operating in ambient argon mixture with oxygen, the more active, hydrophilic, and rough surface was obtained by the plasma-grafting treatments.

1. Introduction

Carbon fiber reinforced polymer composites have been widely used in aerospace, marine, and automobile industries during the past few decades (1960 onwards) because of their engineering properties such as high specific strength and stiffness, lower density, high fatigue endurance, high damping, low thermal coefficient (in fiber direction), etc. [1]. The mechanical properties of carbon fibers reinforced polymer composites are mainly controlled by the interfacial properties between the fiber and the matrix even though they are also affected by the original nature of the fiber and the matrix resin. However, as reinforcements for manufacturing high-performance composite materials, carbon fibers have poor hygroscopicity and adsorption with most polymers because carbon fiber (CF) surface is nonpolar and a compound of highly crystallized graphitic basal planes with an inert structure [2].

As a result, the interfacial bonding strength between the fibers and polymer matrices is low, and excellent mechanical performance of the composites cannot be received [3–5]. Carbon fibers, without any surface treatment, cause a weak adhesion to the matrix resin. To improve the interfacial bonding intensities between the fiber and the matrix, many surface-treatment techniques were developed, including thermal treatment [6], wet chemical or electrochemical oxidation [7,8], plasma treatment [9], gas-phase oxidation [10], ultrasonic bombardment [11], rare earth treatment [12], coating treatment [13], irradiation treatment [4], and so on. However, many of these methods have the drawbacks of high energy consumption, more time consumption, environmental pollution, and in most cases, accompanied by a decrease in fiber strength [14]. Plasma-grafting polymerization method is relatively more convenient, more environmentally friendly, with less impact on the fiber bulk properties [15].

The plasma-induced grafting polymerization onto different types of materials is reported to have a wide range of application in various fields [16–18]. For example, silicone rubber membrane grafted with phospholipid, *n*-isopropylacrylamide was grafted onto

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thermo-responsive polyester fabrics, poly(acrylic acid) grafted on polyhydroxyalkanoate films. Plasma-grafting polymerization method is an effective technique for the surface modification of polymers with plasma because the functional groups desired are able to be definitely introduced on the surface [2]. However, most of the research was not focused much on the performance impact of carbon fibers via the plasma-induced grafting polymerization. Therefore, an attempt has been made to graft maleic anhydride onto the carbon fiber surface by the DBD plasma activated to improve the physicochemical properties of the carbon fiber surface.

In this work, a method has been introduced to obtain strong adhesion between the carbon fiber and epoxy resin through the formation of covalent bonds. Anhydride groups are introduced onto the surface of the fiber by means of plasma-grafting polymerization and then are reacted with the epoxy resin containing curing agent to form covalent bonds. The adhesive property between the grafted fiber and the epoxy resin is assessed using single-fiber fragment test.

2. Experiment

2.1. Materials

TORAYPAN-based T300SC carbon fibers were used. The average diameter is approximately 7 μm, and the typical tensile modulus and strength were about 240 GPa and 3.5 GPa, respectively. The carbon fibers were cleaned in a Soxhlet extractor with acetone for 24 h to remove the size on the fiber surface before experiment. The epoxy matrix system for preparation of the SFC specimens was RIM 145. The graft polymerization was maleic anhydride solution, which dissolved in dimethylbenzene with different concentrations.

2.2. Experiments and conditions

The atmospheric pressure plasma treatments were conducted using a DBD operation. Two circular copper electrodes (diameter = 50 mm) were placed in the DBD plasma configuration. Each electrode was covered with a ceramic plate with a thickness of 2.2 mm and area of $90 \times 90\ mm^2$. Samples were first placed on the lower ceramic plate. When discharged, a large number of dense filamentary microdischarges generated from the upper electrode and bombarded the surface of the samples. Air (20% oxygen and 80% argon) was used as the process gas under the power of 120 W with the 90 s treat time.

Plasma-grafting polymerization has several stages. First, the cleaned carbon fibers were irradiated for 90 s with plasma that were generated at discharge powers of 120 W in an air atmosphere. Second, the plasma-activated carbon fibers were immersed into maleic anhydride solution of different concentrations and stirred by ultrasonic irradiation at 60 °C for 30 min. Finally, the activated groups of carbon fibers and the anhydride groups of polymerization reacted in vacuum at 170 °C for 5 min. The plasma-grafted carbon fibers were washed with pure water under ultrasonic irradiation and then dried 1 h under vacuum at 80 °C.

2.3. Experimental tests

2.3.1. Tests with various grafting rates

The carbon fibers treated by plasma-grafting polymerization are put into dimethylbenzene. Some better test conditions were: a thermal reflux time of 1 h and then cooling, adding 10 N potassium hydroxide–alcohol into the sample solution, using phenothalinas indication agent and a titrate with hydrochloride–isopropyl alcohol to determine the content of graft polymerization.

Table 1
Surface energy of plasma treated carbon fiber at room temperature.

Samples	γ (mJ/m^2)	γ_d (mJ/m^2)	γ_p (mJ/m^2)
Original fiber	49.97	40.79	9.18
Grafted with MAH without plasma treated	52.16	42.79	9.37
Plasma-treated	53.24	43.56	9.68
Plasma-treated grafted with MAH	59.22	48.10	11.12

2.3.2. Contact angle and surface energy

The surface free energy and contact angles of carbon fibers were measured by a DCAT II contact angle measuring device (Dtaphysics Instruments, Filderstadt, Germany). The contact angle of a test liquid on the fiber was measured by the modified Wilhelmy technique using a microbalance. Distilled water and ethylene glycol were used as test liquids as shown in Table 1. The advancing (θ_a) and receding (θ_r) contact angles were calculated from the mass change Δm during the immersion and emersion of the fibers into and from each test liquid by the Wilhelmy equation.

$$\cos\theta = \frac{\Delta mg}{\prod d_f \gamma_l}$$

where γ_l is the surface tension of the test liquid and d_f is the diameter of the carbon fiber estimated from micrographs. The mass change of a single carbon fiber during the measurement was so small that 10 fibers were aligned parallel to each other at an interfiber distance of about 1 mm onto a measuring carrier and tested at a low-stage velocity of 8 μm/s. At least 5 specimens were measured for each treatment group. Fiber surface free energy, which can be divided into two components: dispersive and polar, were derived from the following equations:

$$\gamma_l(1+\cos\theta) = 2\sqrt{\gamma_s^p \gamma_l^p} + 2\sqrt{\gamma_s^d \gamma_l^d}$$

$$\gamma_s = \gamma_s^p + \gamma_s^d$$

where γ_l stands for surface tension of the testing liquid, γ_s stands for total surface free energy of the fiber, and γ_s^p and γ_s^d are the polar component and the dispersive component of the total surface free energy, respectively.

2.3.3. X-ray photoelectron spectroscopy (XPS)

XPS analysis was used to determine the chemical changes on the carbon fiber surfaces introduced by plasma treatment. XPS measurements were carried out on a PHI-1600 X-ray Photo electron Spectroscope (PE Company, USA) at 250 W. The nonmonochromatic Al Kα X-ray radiation ($h\nu$ = 1486.6 eV) was used for excitation. The working pressure in the analyzing chamber was in the range of 5.0E10–9 mbar. Correction of the energy shift due to the static charging of the samples was accomplished with the C1s peak at 285.0 eV as a reference.

2.3.4. SFC test [19]

The influence of a different treatment on the tensile strength of carbon fibers was determined by single filament tensile tests using an XQ-2 single fiber tensile tester (Shanghai Lipu Research Institute, Shanghai, China) equipped with a 2 N load cell. The tensile strength of the carbon fibers was measured at 10 mm gauge lengths at the rate of 0.01 mm/s. Each sample contained at least 30 specimens. The two-parameter Weibull distribution function was adapted to evaluate the injury probability of the carbon fibers. Set $\ln\ln[1/(1-F)]$ as Y axis, and $\ln\sigma$ as X axis. All the Weibull plots and linear fitted lines were obtained. The shape parameter λ and scale parameter σ could be calculated from the slope and intercept of the fitted line.