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Air dielectric barrier discharges plasma surface treatment of three-dimensional braided carbon fiber reinforced epoxy composites

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ABSTRACT

The deposition of coatings on the surface of three-dimensional braided carbon fiber reinforced epoxy (C_{3D}/EP) composites will be helpful to their applications. However, they are unsuitable to be deposited due to their low surface free energies, poor wettabilities and poor adhesions. Since treatment of polymers or composites by non-thermal plasmas is a fast, versatile and environmentally friendly surface modification technique, the plasma treatment of C_{3D}/EP composites is investigated in this paper. Dielectric barrier discharges (DBD) in ambient air are used. C_{3D}/EP (V_f=36%) samples with thickness of 2 mm are placed into the plasma configuration. Time for plasma treatment is 30 s, 60 s and 120 s. The chemical and physical changes induced by the treatments on C_{3D}/EP surface are examined using contact angle measurements, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The water advancing contact angles of the plasma-treated C_{3D}/EP samples change from 98.6° for the untreated sample to the lower value 45.7° after plasma treatment of 30 s and 42.7° of 120 s. XPS results reveal that the composites modified with the DBD at an atmospheric pressure show a significant increase in oxygen-containing and nitrogen-containing groups, such as C–O, O–C=O and NO_2. The AFM images of the untreated and plasma-treated C_{3D}/EP samples show that the composites surfaces roughen. The roughness of the untreated C_{3D}/EP is 1.6 nm, while after plasma treatment of 30 s, 60 s and 120 s the values are 2.4 nm, 3.0 nm and 3.9 nm respectively. These results demonstrate that the surfaces of the C_{3D}/EP samples are more active, hydrophilic and rough after plasma treatments using a DBD operating in ambient air.

1. Introduction

Fiber reinforced polymer composites have been used widely in aerospace, marine and automobile industries during the past few decades (1960 onwards) due to their good engineering properties such as high specific strength and stiffness, lower density, high fatigue endurance, high damping and low thermal coefficient (in fiber direction), etc [1]. Three-dimensional braided carbon fiber reinforced epoxy (C_{3D}/EP) composites are excellent materials for surgery or aviation because of their good properties, such as improved overall performance, high strength, desirable modulus, splendid friction and wear characteristics, etc [2,3]. The deposition of some coatings on the surface of C_{3D}/EP composites will be greatly helpful to their applications. However, C_{3D}/EP composites are unsuitable to be deposited due to their low surface free energies, poor wettabilities and poor adhesions. As a result, surface modification of C_{3D}/EP composites is quite required. Treatment of polymers or composites by non-thermal plasmas has become more and more popular as a surface modification technique, since it is a fast, versatile and environmentally friendly method [4].

Application of plasma technologies in fiber reinforced composites is mainly focus on cleaning and roughening of fibers in order to enhance the fiber-matrix adhesion [4–6], treatment of the fracture surface as a means for exposing filler particles in the fracture surface [7,8] or treatment of membranes [9]. There are comparatively a few studies on the plasma surface treatment of the thick composite materials [10]. Zhang [11] studied the tribological behavior of the argon plasma-treated carbon fiber reinforced PEEK composites. Meyer [5] carried out surface etching of three dimensional shaped parts of carbon fiber reinforced epoxy and PEEK composites by plasma etching with an O_2 and C_2F_6 mixture. Kim et al. [6,12] investigated the surface of carbon/epoxy layers of prepregs by examining the strength of single lap composite adhesive joint after argon plasma or oxygen plasma treatment. Kyong [13] inspected the peel strength and the shear strength of aluminum/CFRP composites in which the surface of the aluminum was treated using DC plasma and the surface of the CFRP was treated by Ar^+ ion assisted reaction method under oxygen environment. However, there are few reports of atmospheric pressure air dielectric barrier discharges (DBD) plasma treatment of fiber reinforced polymer composites surfaces even if this treatment is more economical than other plasma treatments because it need no special gas and subsequent special equipments. Otherwise, morphology of three-dimensional braided composites surfaces after polishing is different to normal composites. Therefore, it is necessary to investigate the atmospheric pressure air DBD plasma treatment of three-dimensional braided fiber reinforced polymer composites surfaces.

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The atmospheric pressure air DBD plasma treatment of C_{3D}/EP composites is investigated in this paper and the chemical and physical changes induced by the treatments on C_{3D}/EP surface are examined using contact angle measurements, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM).

2. Materials and methods

2.1. Materials and surface treatment

The samples were C_{3D}/EP composites prepared through RTM (resin transfer molding) process. The concentration of carbon fiber was 36 vol.% and that of epoxy resin was 64 vol.%. Samples were of the thickness of 2 mm and rectangular shape. They have been mechanically polished up to obtain a mirror-like surface and then cleaned by ultrasonic wave for 30 min.

The atmospheric pressure plasma treatments were performed using a DBD operating in air. Two circular copper electrodes (diameter = 150 mm) were placed in the DBD plasma configuration. Each electrode was covered with a quartz glass plate with thickness of 2 mm and circular area of 210 mm diameter. The gas gap between the two quartz glass plates was 6 mm. Before starting the experiments, samples were placed on the lower quartz glass plate.

The pulsed types AC power supply presented voltage whose voltage was 8 kV and frequency was 8 kHz. The discharge current was 40 mA and peak pulse current was 300 mA. When discharged, a large number of dense filamentary microdischarges generated from upper electrode and bombarded the surface of samples. Time for plasma treatment was 30 s, 60 s and 120 s.

2.2. Contact angle measurements

Surface wettability and hydrophilicity of the C_{3D}/EP sample were investigated by advancing and receding contact angle measurements. Contact angles were obtained using a DCAT21 contact angle measuring device (Dataphysics company—Germany). Distilled water was used as test liquids.

2.3. X-ray photoelectron spectroscopy (XPS)

XPS analysis was used to determine the chemical changes on the C_{3D}/EP surfaces introduced by plasma treatment. XPS measurements were carried out on a PHI-1600 X-ray Photoelectron Spectroscope (PE company—USA) operated at 250 W. The non-monochromatic Mg K_α X-ray radiation (hv = 1486.6 eV) was used for excitation. The working pressure in the analyzing chamber was in the range of 10^{-8}–10^{-9} Torr. Correction of the energy shift due to the static charging of the samples was accomplished with the C1s peak at 284.6 eV as a reference.

2.4. Atomic force microscopy (AFM)

AFM images were obtained by a Nanoscope IIIa atomic force microscope (DI company—USA). The surface topology and the root mean square (RMS) roughness were recorded and analyzed.

3. Results and discussion

3.1. Contact angle measurements

The advancing/receding contact angle measurement method, which quantifies hysteresis, is especially suited for understanding the surface wettability and controlling the surface wetting behavior [14]. Table 1 indicates the effects of discharge time on contact angles against water. With time for treatment prolongs, it is observed that advancing angle of C_{3D}/EP sample is on the decrease, especially in the first 30 s. It changes from 98.56° for the untreated sample to the lower value 45.65° after plasma treatment of 30 s. After 60 s and 120 s discharges, the advancing angles reduce to 43.73° and 42.73° respectively. So it can be seen that saturation of the surface modification reaches after 30 s exposure.

Table 1
Contact angle of C_{3D}/EP surfaces untreated and after plasma treatment for multiple times

Time for plasma treatment (s)	Contact angle of C_{3D}/EP surfaces		
	Advancing angle (deg)	Receding angle (deg)	Contact angle hysteresis (deg)
0	98.56	20.26	78.30
30	45.65	13.49	32.16
60	43.73	21.98	21.75
120	42.73	22.04	20.69

It is known that the advancing contact angle is less sensitive to surface roughness and heterogeneity than the receding angle and therefore commonly used to calculate surface and interfacial tension components, which are vital to indicate surface wettability and hydrophilicity [15]. Table 1 shows that advancing contact angles of C_{3D}/EP surface reduce with treatment time increasing, which reveal that surface wettability and hydrophilicity of C_{3D}/EP surface are enhanced with treatment time increasing. This can be explained by the changes of surface topology and chemical compositions (see Sections 3.2 and 3.3).

As can be seen in Table 1, the receding angle of the untreated C_{3D}/EP surface (20.26°) reduces to 13.49° after 30 s plasma treatment and then raises to 21.98° and 22.04° respectively after 60 s and 120 s discharges.

The advancing contact angle is more sensitive to the hydrophobic component while the receding angle is more sensitive to the hydrophilic one if the surface is made up of heterogeneous components [14]. The difference between the advancing and receding contact angles is known as the contact angle hysteresis [16].

Table 1 shows the contact angle hysteresis of C_{3D}/EP surfaces. The contact angle hysteresis of the plasma-treated C_{3D}/EP sample changes from 78.30° for the untreated sample to 32.16° after plasma treatment of 30 s. After 60 s and 120 s discharges, the contact angle hysteresis are 21.75° and 20.69° respectively.

Contact angle hysteresis has been attributed to solid surface roughness, surface heterogeneity, and some other surface chemical properties [17–21]. But surface roughness is not expected to result in contact angle hysteresis for surfaces with roughness at the nano-scale level [14,17]. A number of studies [18–20] have reported that surface chemical heterogeneities, surface swelling, penetration of liquid into the solid surface, and surface reorientation of chemical functional groups can all lead to contact angle hysteresis. In this paper, C_{3D}/EP surface is made up of two regularly interlaced areas. They are epoxy, whose concentration is 64% or more, and exposed carbon fiber areas. When plasma treated, C_{3D}/EP surface, including epoxy and carbon fiber areas, is more active and rough with time for treatment prolongs (see Sections 3.2 and 3.3). These can reduce heterogeneity of carbon fiber and epoxy on the surfaces of composites because exposed carbon fiber areas, which are less hydrophilic than epoxy originally, become more active and meanwhile the epoxy areas, which are less rough than carbon fiber areas originally, become rougher. The reduction of surface heterogeneity is one of the reasons of contact angle hysteresis decreasing. Otherwise, Gong [21] found that PVA-p-PDAmC10 LB film has a very large contact angle hysteresis (>80°), which means that reorientation of the surface configuration takes place dramatically, and the hysteresis can be greatly reduced (<30°) by UV-irradiation due to the photocycloaddition in the side chains of PVA-p-PDAmC10. Because of the similar contact angle hysteresis results, reorientation of C_{3D}/EP surface is under suspicion of decreasing after plasma treatment and becoming another reason of contact angle hysteresis reducing.

3.2. XPS analysis

XPS survey spectra of untreated and plasma treated C_{3D}/EP surfaces show similar photoelectron peaks attributed to C, O and N.