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Improvement of atomic oxygen erosion resistance of carbon fiber and carbon fiber/epoxy composite interface with a silane coupling agent

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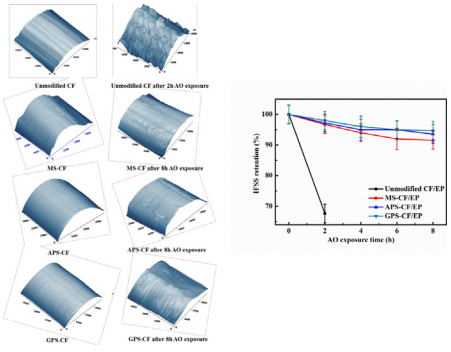
HIGHLIGHTS

- A facile method to improve atomic oxygen erosion resistance for the interface of carbon fiber/epoxy composites was proposed.
- Three types of silane coupling agents with different ending groups were used to investigate their effect on the AO erosion resistance.
- Both the interfacial adhesion and AO erosion resistance ability of CF/EP composites had an obvious improvement through the generation of SiO_2 on the interface of composites.

GRAPHICAL ABSTRACT



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ABSTRACT

It is critical for carbon fiber/epoxy (CF/EP) composites to have a high resistance to atomic oxygen (AO) erosion when they are utilized in a low earth orbit (LEO) environment. Herein, we proposed a simple method whereby a silane coupling agent (SCA) was applied onto the carbon fiber surface to fabricate CF/EP composites with both improved interfacial shear strength (IFSS) and AO erosion resistance. The SCA was first hydrolyzed, then reacted with the hydroxyl groups on the pretreated CF surface, and finally formed a continuous uniform layer of siloxane oligomers. Atomic force microscopy images exhibited relatively smooth surfaces for SCA-treated CFs after AO erosion, when compared to the rough surface for bare CFs. It was found that the IFSS and AO erosion resistance were improved for SCA-coated CFs and CF/EP composite interface since a silica (SiO_2) layer was formed upon exposure to AO as confirmed by XPS results.

1. Introduction

Owing to the low density, good electrical conductivity, high specific strength and modulus [1–2], carbon fiber/epoxy (CF/EP) composites are widely used as spacecraft materials. However, when a spacecraft operates in a low earth orbit (LEO) at altitudes between 200 and 700 km, many environmental factors, such as atomic oxygen (AO), high-energy ultraviolet (UV), vacuum ultra violet (VUV), thermal cycling, micro-meteoroid and space debris, can severely impact the material and affect its structural reliability and lifetime [3,4]. Among these, AO with high chemical reactivity is regarded as the most dominant

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and harsh species [5]. Although the density of AO is not high in the LEO, the high orbital speed of the spacecraft can still lead to high AO fluxes (10^{14}–10^{15} atoms/cm^{2}s) and high collision energies (ca 5 eV) [6]. When AO attacks composite materials, the interactions between them are quite complex. For example, AO (a) can scatter over the composites without chemical reaction, (b) reacts with composite surface forming volatile oxides like carbon oxide and nitrogen oxide, and (c) penetrates into and damages the composites [7]. Particularly, for CF/EP composites, AO can interact with both the carbon fiber and epoxy matrix. The reaction with CF generally leads to the formation of volatile oxides on the surface resulting in surface recession. Degradation of the epoxy matrix under AO attack also causes significant mass loss and irreversible reductions of physical and chemical properties [8,9] due to polymer bond breakages and thence molecule fragmentations leading to the erosion of the epoxy matrix.

Hence, CF/EP composites are vulnerable to AO exposure, which affects their performance and may even cause material failure. So, it is critical to fabricate CF/EP composites with high resistance to AO erosion. To this end, many approaches have been developed, such as surface protective coating (e.g., SiO_2, Al_2O_3) [10–12], surface modification (e.g., ion implantation) [13,14], and incorporation of nanofiller (e.g., CNTs, SiO_2, graphene) in epoxy matrix [15–17]. While these methods can, to some degree, protect the composites from AO erosion, the interface between CF and epoxy is rarely investigated even though a fiber-matrix interface with good bonding is required for effective load transfer from matrix to fiber [18] to achieve the ultimate mechanical performance of the composite.

When CF/EP composites are used in LEO under thermal cycling, cracks occur inevitably at the interface due to the differential thermal expansion between CF and epoxy matrix. Once AO concentrates inside these cracks, the ensuing interface failure may even tear off the CF/EP composite leaving the CF fully exposed and severely corroded [19]. To address this problem, it is necessary to achieve improved interfacial adhesion and enhanced AO erosion resistance for the interface of CF/EP composites and the CFs.

In our previous work, Wei et al. [20] applied gold (Au) coating on CF surface to protect the interface of CF/EP composites and it was found that the untreated composite interface was severely eroded by AO and its interface shear strength (IFSS) decreased dramatically with the greatest loss of 13.0 MPa/h, while the interface treated by Au coating could retain 95% of the IFSS value after 8 h exposure. However, the Au-coated CF sacrificed the interfacial adhesion between CF and epoxy due to the incompatibility between Au and epoxy. He et al. [21] further introduced a thiol self-assembly film on the Au-coated CF surface to improve the interfacial resistance against AO erosion. Although this method solved the problem of a weak interfacial adhesion and further increased the AO erosion resistance with the highest IFSS retention of 96.3% compared to an Au-coated interface, Au-coating is prohibitively expensive. By contrast, silane coupling agent (SCA) treatment is a practical economic method widely used to enhance interfacial adhesion in fiber reinforced composites, where SCA can react with fiber and epoxy based on their bifunctional groups thereby forming chemical bridges between themselves [22,23]. However, its influence on AO erosion resistance is, to our best knowledge, not studied. In fact, SCA can be oxidized to form silica (SiO_2) that is inert to AO and thus acts as a barrier to CFs in the composites.

Here, in this paper, we proposed a SCA treatment method to improve the interfacial interaction and AO erosion resistance for the interface of CF/EP composites. Carbon fiber was first modified with three types of SCA having different end groups. Then, the effects of AO attack on the mechanical properties of SCA-treated carbon fibers and the interface of CF/EP composites were studied under a ground simulation AO facility. The interfacial shear strength (IFSS) was chosen to evaluate the interfacial property and the AO resistance of the composite interface. It was found that after SCA-treatment, the IFSS was much increased and showed very good retention after AO exposure.

2. Experimental work

2.1. Materials

T300 carbon fibers were provided by Toray Company, Japan. The matrix was epoxy resin E-51 and hardener H-256. Three types of silane coupling agents, viz., methyltrimethoxysilane ($CH_3Si(OCH_3)_3$, MS, 96%), γ-aminopropyltriethoxysilane ($H_2N(CH_2)_3Si(OC_2H_5)_3$, APS, 97%) and γ-glycidoxypropyltrimethoxysilane ($CH_2OCHCH_2O(CH_2)_3Si(OCH_3)_3$, GPS, 99%), were purchased from Aldrich Chemical Co. These SCAs with different end groups possess different reactivity with the epoxy matrix. Other chemical reagents including nitric acid (HNO_3), lithium aluminum hydride ($LiAlH_4$), tetrahydrofuran (THF), acetone and ethanol (96%) were obtained from Sinopharm Group Co., Ltd.

2.2. Preparation of SCA modified carbon fibers

Surface sizing and contaminants on carbon fibers were removed using acetone at 70 °C for 48 h. Then, CFs were pretreated to obtain hydroxylated fibers by three steps: (a) oxidizing in HNO_3 (6 M, 100 ml) for 1 h at 80 °C, (b) reducing in $LiAlH_4$-THF saturated solution for 1 h, and (c) rinsing with deionized water and drying at 100 °C for 10 min. The SCA solution was prepared by dissolving three types of SCAs (MS, APS and GPS) (1 ml) in 100 ml ethanol at room temperature by vigorous stirring. The as-prepared hydroxylated CFs were separately immersed into each of three SCA-ethanol solution and were then stirred at ambient conditions for 8 h. Finally, the SCA modified CFs were obtained after rinsing with deionized water and drying at 80 °C, and they were designated as MS-CF, APS-CF and GPS-CF, respectively.

2.3. Preparation of SCA modified CF/EP composites

Microbond samples for IFSS tests were prepared by dripping epoxy resin droplets onto a SCA modified CF monofilament with an embedded length of 60–80 μm, followed by curing first at 80 °C for 1 h, then at 120 °C for 2 h, and finally at 150 °C for 3 h. For convenience of description, samples from these three types of composites are named: MS-CF/EP, APS-CF/EP and GPS-CF/EP. For comparison, bare CF/EP samples were also prepared as controls.

2.4. Experiments on AO exposure

The AO exposure experiments were conducted on a ground-based AO effects simulation facility at Beihang University, Beijing. The working principle of this facility is as follows. First, the oxygen influx into a vacuum chamber is controlled to reach a certain working pressure; second, the cathode filament is heated electrically. As the temperature and discharging voltage between filament and vacuum chamber walls increase, electrons are emitted from the surface of the cathode filament and reach a sufficiently high-energy level. Third, the oxygen plasma is formed through the collision ionizations and dissociation of oxygen molecules by the electrons. The main components of the plasma are O_2, O_2^+, O, O^+ and e^-, which impinge on the samples during the experiment. Among these, atomic oxygen O is the dominant component owing to its strongest characteristic spectral band. More details on the configuration and characteristics of the facility can be found elsewhere [24]. In our experiments, unmodified and SCA modified CF monofilaments and CF/epoxy microbond samples were first attached to a concave iron holder (7×2 mm^2), and then vertically placed in another circular holder with a diameter of 160 mm in the vacuum chamber for AO exposure. The temperature and pressure in the system were 60–70 °C and 1.4×10^{-1} Pa, respectively. Kapton, a commonly applied polymer for spacecraft, can be severely eroded by AO and its erosion yield is a constant [25]. Thus, it was chosen as the standard material to calculate the AO flux through its mass loss. AO exposure time for various samples