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Chemical alteration of poly(vinyl fluoride) Tedlar® induced by exposure to vacuum ultraviolet radiation

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Abstract

In this study the chemical alteration of poly(vinyl fluoride) Tedlar® by vacuum ultraviolet radiation (VUV) (115–400 nm) has been examined using X-ray photoelectron spectroscopy (XPS). The initial F/C atom ratio of 0.34 decreases to 0.17 after a 2-h exposure. The F/C atom ratio is further reduced to a steady-state value of approximately 0.04 after a 24-h exposure. Similarly, the O/C atom ratio is reduced from 0.08 to 0.05 and then to 0.02 during these two exposures. As the F and O are removed by VUV exposure, the C concentration increases from 70.5 to 82.0 and then to 94.6 at.% thus forming a graphitic or amorphous carbon-like layer which erodes more slowly than the virgin Tedlar surface. Exposure of the VUV-damaged surface to O_2 results in chemisorption of O, indicating that reactive sites are formed during the chemical erosion by VUV. Further exposure to VUV removes this chemisorbed oxygen but a subsequent exposure to air at atmospheric conditions causes a three-fold increase in O chemisorbed at the surface. Comparison of XPS data indicates that the mechanisms of chemical alteration by VUV radiation and hyperthermal (~5 eV) atomic oxygen (AO) are similar.

Keywords: Fluoromers; Fluoropolymers; Teflon; Tedlar; Tefzel; XPS; AO; VUV; Low earth orbit; LEO

1. Introduction

Polymers are attractive and desirable materials for use in space applications, because they are lightweight and typically much easier to process using techniques such as extrusion, casting and injection molding at relatively low temperatures compared to metals and ceramics. They also tend to be more flexible and offer a wide variety of choices from optically transparent to opaque, rubbery to stiff and conducting to insulating. Fluoroethylene propylene (FEP) Teflon® [1] is one material that is widely used as a thermal blanket for spacecraft flying in low-earth orbit (LEO) [2]. Thermal control is provided by lining the FEP Teflon with aluminum or silver. Since FEP Teflon has a high thermal emittance, this system reflects a large fraction of the incident solar energy.

However, over the last two decades, it has been well established that polymers undergo severe degradation

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resulting in reduced spacecraft lifetimes. These materials degrade because spacecraft surfaces are exposed to high fluxes of hyperthermal atomic oxygen (AO), bombardment by low- and high-energy charged particles, thermal cycling and the full spectrum of solar radiation including UV. AO is the main constituent of the atmosphere in LEO. It is formed by dissociation of O_2 by ultraviolet radiation from the sun, resulting in an AO concentration of approximately 10^8 atoms/cm^3. The actual flux of $\sim10^{14}$ atoms/cm^2 s impinging on a spacecraft is high due to orbiting speeds of approximately 8 km/s. At these relative speeds thermal AO collides with a kinetic energy of ~4.5 eV. These highly energetic collisions not only result in surface chemical reactions but also lead to a pure physical sputtering of the surface atoms. Many studies have been conducted in an effort to determine the mechanism of degradation caused by surface reactions with AO [3–10]. However, these studies have all been carried out after exposing these highly reactive surfaces to air prior to analysis, thus introducing the possibility of artifacts that do not represent the true space environment. A recent study has shown that exposure to air chemically alters the reactive surfaces formed during AO exposure [11]. It is, therefore, essential that analysis of polymers exposed to AO be carried out in vacuo to avoid artifacts induced by air exposure.

Several studies have been conducted on the deterioration of fluorinated polymers retrieved from spacecraft subjected to the LEO environment. The outer layer of FEP Teflon multi-layer insulation on the Hubble space telescope (HST) was significantly cracked at the time of the second HST servicing mission, 6.8 years after it was launched into LEO [12,13]. Comparatively, minor embrittlement and cracking were also observed in the materials retrieved from solar-facing surfaces on the HST at the time of the first servicing mission (3.6 years of exposure to LEO). Furthermore, an increased deterioration of fluorinated polymers may result from a synergistic effect of vacuum ultraviolet (VUV) radiation and charged particles such as electrons and ions in the presence of AO [14]. This point will be examined in future studies.

The goal of this study is to examine and attempt to understand the chemical alterations of a Tedlar surface when impacted by VUV radiation. The source used is described below. There are three types of bonds in Tedlar; C–C bonds, C–H bonds and C–F bonds with approximate bond strengths of 83, 105 and 111 kcal/mol, respectively. The VUV radiation used in this study is energetic enough to break these bonds. A single Tedlar surface was exposed to VUV for various time periods and then exposed to research-grade O_2 to test the chemical reactivity of the VUV-exposed surface. Then the same surface was exposed to VUV and to air. Finally, it was exposed to VUV for an extended period to obtain a steady-state composition. A similar set of experiments have been carried out on Tedlar using AO [15], and the results of these experiments are compared with the results of this present study. Future studies are planned in which fluoropolymer surfaces will be exposed simultaneously to both AO and VUV radiation to simulate the space environment.

This study is part of a larger study in which the goals are to characterize the effects of LEO on various types of polymers and to develop new polymers which will withstand the effects of LEO. Kapton® [1] is widely used as a thermal blanket for spacecraft, but it erodes severely in LEO. A study has been carried out in which Kapton was exposed to hyperthermal AO [11]. XPS data indicate that the initial attack site is the carbonyl portion of the Kapton by reaction with AO to form CO_2, which desorbs. This results in a reduction of the O content in the near-surface region. The Kapton surface becomes quite rough during AO exposure according to images taken using atomic force microscopy (AFM). Exposure of Kapton to 1-keV He^+ also results in lowering the C and N surface contents [16]. AO exposure studies have also been carried out on polyhedral oligomeric silsesquioxane (POSS)-containing copolymers [17–20]. These are particularly interesting systems because when exposed to hyperthermal AO, the C and H are removed leaving a thin layer (~30 Å) of SiO_2 which protects the underlying polymer from further erosion. This structure is also self-repairing in that SiO_2 forms again if the original layer is damaged.

A study was carried out by Pruden et al. [21] in which parylene-N and parylene-C was exposed simultaneously to oxygen and ultraviolet light. Using XPS and other surface-sensitive techniques, they found that aldehyde and carboxylic acid groups form in the near-surface region. Shyichuk et al. [22] have