Effects of Vacuum Ultraviolet Radiation on Atomic Oxygen Erosion of Polysiloxane/SiO$_2$ Hybrid Coatings

Longfei Hu[1,2], *Meishuan Li*[1]† *and Yanchun Zhou*[1]

1) Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China
2) Graduate School of Chinese Academy of Sciences, Beijing 100039, China

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Polysiloxane/SiO$_2$ hybrid coatings have been prepared on Kapton films by a sol-gel process. The erosion resistance of polysiloxane/SiO$_2$ (20 wt pct) coating was evaluated by exposure tests of vacuum ultraviolet radiation (VUV) and atomic oxygen beam (AO) in a ground-based simulation facility. The experimental results indicate that this coating exhibits better AO resistance than pure polysiloxane coating. The erosion yield (E_y) of the polysiloxane/SiO$_2$ (20 wt pct) hybrid coating is about 10^{-27} cm^3/atom, being one or two orders of magnitude lower than that of polysiloxane. VUV radiation can affect the erosion process greatly. Under simultaneous AO and VUV exposure, the value of E_y of the polysiloxane/SiO$_2$ (20 wt pct) hybrid coating increases by 39% compared with that under single AO exposure.

KEY WORDS: Atomic oxygen; Vacuum ultraviolet radiation; Erosion yield; Hybrid coating

1. Introduction

Spacecraft or space structures experience harsh environments in low-earth-orbit (LEO) at altitudes between 200 and 700 km, such as high flux of atomic oxygen (AO), charged particles, thermal cycling, and full spectrum of solar radiation[1,2]. Because AO is highly oxidative and can directly react with space materials, and its flux and kinetic energy can reach 10^{12}–10^{15} atoms/(cm^2·s) and 5 eV, respectively for a spacecraft at orbiting speed of 7–8 km/s[3], attacks of AO can cause severe damages of polymer materials in space structures, and affect the performance and service life of spacecrafts significantly. Moreover, vacuum ultraviolet radiation (VUV) can also result in degradation of polymer materials. In the existence of VUV, attacks of AO become more harmful[4,5].

In order to improve AO resistance of space materials, various protective coatings, such as inorganic coatings (SiO$_2$, amorphous Si), organic coatings (silicones, fluoropolymers), and organic-inorganic hybrid coatings have been developed[6–9]. Usually, inorganic coatings have excellent AO resistance and are insusceptible to VUV radiation, but crack easily due to their intrinsic brittleness. Organic coatings possess good AO erosion resistance, ductility, and processability, but they are susceptible to VUV radiation. Thus, organic-inorganic hybrid coatings[7–10] are proposed, which combine the advantages of both inorganic coatings and organic coatings. David and Mark[9] prepared polysiloxane/meatal-oxo-clusters hybrid, and demonstrated its excellent AO resistance as protective space coatings. Banks et al.[10] tested the AO resistance of thin polysiloxane/silicon-oxo-clusters hybrid coatings, and found that these coatings could greatly reduce surface shrinkage tendency of polysiloxane during atomic oxygen plasma exposure. Duo et al.[11] examined the resistance of polyimide/SiO$_2$ (20 wt pct) hybrid film to AO attack, and demonstrated that

its erosion yield (4.0×10^{-26} cm^3/atom) was two orders of magnitude lower than that of polyimide film (3.0×10^{-24} cm^3/atom). However, the effects of VUV on AO erosion of hybrid coatings have not been reported. Because organic constituent is taken as matrix in these hybrid coatings, it is necessary to evaluate their resistance to VUV and AO attack.

In this paper, polysiloxane/SiO$_2$ hybrid coatings were prepared by sol-gel process. The erosion resistance of the polysiloxane/SiO$_2$ (20 wt pct) coating was investigated by exposure tests of VUV radiation and AO beam in a ground-based simulation facility. Synergistic effects of AO and VUV radiation on the degradation of the coating were also discussed.

2. Experimental

2.1 Coating preparation

Polysiloxane and tetraethylorthosilicate [Si(OC$_2$H$_5$)$_4$, 98%, TEOS] were chosen as the starting organic and inorganic compounds, respectively. Xylene was chosen as a solvent. Hydrochloric acid [HCl, 36 wt pct] was used as a catalyst, and KH550 as a coupling agent. The preparation process is quite similar to that introduced by Oh et al[12]. Briefly, the molar ratio of TEOS:C$_2$H$_5$OH:H$_2$O:HCl was selected as 1:1:4:0.1 to prepare a silica precursor solution. Then by tailoring weight ratios of the silica precursor to polysiloxane, polysiloxane/SiO$_2$ hybrid solutions with different SiO$_2$ content were obtained. Finally, these solutions were sprayed on a Kapton substrate and thermally treated in a vacuum furnace at 220°C for 4 h. The thickness of the as-prepared hybrid coating was about 1 μm. In AO exposure experiments, samples with dimensions of 20 mm×20 mm×0.014 mm were used.

2.2 Ground-based simulation facility and exposure tests

Exposure tests of AO/VUV were carried out in a ground-based simulation facility established in our lab. In this facility, a 2.45-GHz microwave source with

† Corresponding author. Prof; Tel.: +86 24 23971145;
 E-mail address: mshli@imr.ac.cn (M.S. Li).

Table 1 Summary of experimental conditions during exposure tests

Vacuum chamber pressure/Pa	O$_2$ flow rate /SCCM	VUV radiant intensity/Suns	[O]:[O$_2$]	Atomic oxygen flux /(atoms/(cm^2·s))
0.04–0.05	4.3	5	85:15	4.5×10^{16}
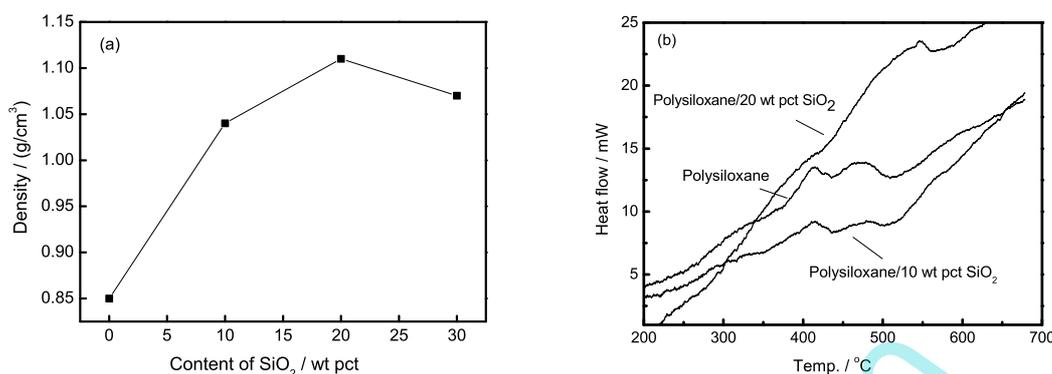
Fig. 1 (a) Density of hybrid solutions and (b) DSC analysis of as-prepared polysiloxane/SiO$_2$ hybrid coatings

a power of 500 W was launched into the circular cavity to generate electron cyclotron resonance (ECR) oxygen plasma. The oxygen ions moved to a negatively biased Mo plate under the electric force and the confining of a symmetrical magnetic mirror field, and then they were neutralized and reflected to form the AO beam. Details about this facility and AO parameters calibration have been reported in our previous work[13]. The AO flux at the sample position was calibrated using a bare Kapton film, which is a current accepted method for determining active particles flux. The incident oxygen atoms were controlled to an energy of ∼5 eV by adjusting the bias on Mo plate. A deuterium lamp with a wavelength of 115–400 nm was used as VUV source. This facility also equipped with a quartz crystal microbalance (QCM) with a sensitivity of 10^{-9} g, so that *in-situ* mass change can be measured simultaneously during exposure tests. When QCM was used, the hybrid coating was prepared on a small disk-like gold resonator beforehand.

In this study, four series of exposure tests were conducted: single VUV exposure, single AO exposure, simultaneous AO and VUV exposure (AO+VUV), 1 h pre-VUV exposure then single AO exposure (VUV-AO). The AO flux and the VUV intensity were 4.5×10^{16} atoms/(cm^2·s) and ∼5 Suns, respectively. Details about experimental conditions are listed in Table 1.

2.3 Characterization of exposed samples

The surface morphologies of sample before and after exposure were observed by scanning electron microscopy (SEM, LEO supra 35, Germany) and atomic force microscopy (AFM, CSPM3100, China). The chemical composition on the surface was determined by X-ray photoelectron spectrometer (XPS, ESCA LAB 250) and Fourier transform infrared spectroscopy (FTIR, Perkin Elmer spectrum one, USA).

3. Results and Discussion

3.1 Characterization of polysiloxane/SiO$_2$ hybrids

Figure 1(a) presents the density variation of the polysiloxane/SiO$_2$ hybrid solutions with SiO$_2$ content and Fig. 1(b) gives the differential scanning calorime-

try (DSC) analysis of the hybrid coatings. The density of the hybrid solutions increases remarkably with addition of SiO$_2$ in the range of 0–20 wt pct, and then decreases slightly with further SiO$_2$ addition. The reason for this phenomenon is that to obtain stable and transparent hybrid solutions, more xylene is needed with increasing SiO$_2$ content. The DSC analysis implies that the decomposition temperature of polysiloxane is not affected by the addition of 10 wt pct SiO$_2$, but increases greatly in the condition of 20 wt pct SiO$_2$ addition.

The adhesion and flexibility of the polysiloxane/SiO$_2$ hybrid coatings were determined by bending coated flat samples around the cylindrical surface of a mandrel with the diameter of 5 or 2 mm. It was confirmed that the coatings possessed good adhesion and flexibility, since no crack or detachment was observed. The cracking and spallation resistance of the coatings were also evaluated through thermal cycling from 150 to −196°C. The samples were heated in a furnace at 150°C for 2 min, and then cooled in liquid nitrogen for 2 min, which was defined as one cycle. After 30 cycles, no cracking occurred, so the coating adhered tightly to the substrate.

Figure 2 shows the cross section morphologies of polysiloxane and polysiloxane/SiO$_2$ (20 wt pct) hybrid, which were prepared on a microscope slide by dropping. The cross section of polysiloxane is uniform. For the hybrid, nano-SiO$_2$ particles appear and distribute evenly in polysiloxane. The surface of the as-prepared polysiloxane/SiO$_2$ (20 wt pct) hybrid coating is smooth and defects free. When the content of silica precursor became higher than 20 wt pct, agglomeration of nano-SiO$_2$ particles took place.

Based on the above experimental tests, the addition of 20 wt pct SiO$_2$ can greatly improve the thermal stability of polysiloxane, and the hybrid solution has a uniform SiO$_2$ particles contribution and maximum density, and therefore the ultimate content of SiO$_2$ in the hybrid is selected as 20 wt pct.

3.2 AO and VUV erosion resistance

3.2.1 Mass loss and erosion yield

Exposure experiments were conducted in the
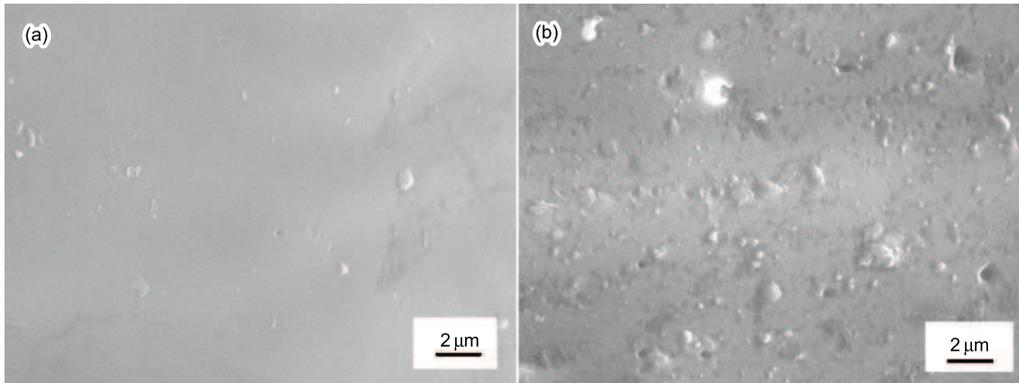
Fig. 2 Cross section morphologies of pure polysiloxane and polysiloxane/SiO$_2$ (20 wt pct) hybrid coating
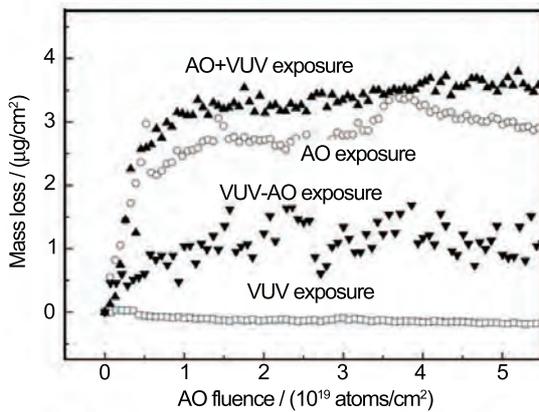
Fig. 3 Mass changes of the polysiloxane/20 wt pct SiO$_2$ hybrid coating under different exposure conditions

ground-based LEO simulator. The erosion kinetics of the polysiloxane/SiO$_2$ (20 wt pct) coating was determined by QCM technique. Frequency shift of the coated disk-like gold resonator was *in-situ* recorded, and the corresponding mass changes were calculated by the following equation:

$$\Delta M/A = \Delta F/(-2.6 \times 10^6 F_0^2) \qquad (1)$$

where ΔM is the mass change of the exposed sample (g), A is the exposed area (cm^2), ΔF is the frequency shift (Hz) and F_0 is the nominal frequency (MHz). Figure 3 illustrates the erosion kinetics under different exposure conditions. During single VUV exposure, a small mass gain was detected, whereas remarkable mass loss was found in exposures to single AO, VUV-AO, and AO+VUV. In these three conditions, the mass loss increased rapidly at the initial exposure stage of 1.0×10^{19} atoms/cm^2 fluence, and then roughly kept a stable value. It can also be seen that in AO+VUV exposure, the mass loss is greater than that in single AO exposure, while in VUV-AO exposure, the mass loss is the smallest.

Based on the above erosion kinetics, the erosion yield of the polysiloxane/SiO$_2$ hybrid coating can be determined through the following equation:

$$E_y = \Delta M/(\rho At F) \qquad (2)$$

where E_y is the erosion yield (cm^3/atom), ΔM is the mass loss of the sample (g), ρ is the density of the

sample (g/cm^3), A is the exposed area of the sample (cm^2), t is the test time (s) and F is the AO flux (atoms/(cm^2·s)). In this study, the average erosion yield of the polysiloxane/20 wt pct SiO$_2$ coating was 7.2×10^{-27}, 2.7×10^{-27}, and 10×10^{-27} cm^3/atom under AO, VUV-AO, and AO+VUV exposure, respectively. These values are one or two orders of magnitude lower than that of polysiloxane coatings (10^{-25}–10^{-26} cm^3/atom)[14,15]. During AO+VUV exposure, the value of E_y becomes 39% higher than that during single AO exposure.

3.2.2 Surface morphologies

SEM images of the exposed polysiloxane and polysiloxane/SiO$_2$ hybrid coating are displayed in Fig. 4. Before exposure, the two coatings showed a smooth and crack free surface. After AO exposure, the polysiloxane coating shrank and many surface microcracks could be detected clearly (Fig. 4(a)); the hybrid coating (20 wt pct), however, showed an intact surface with obvious appearance of nanoparticles (Fig. 4(b)), surface shrinkage or cracks were not found. Hence it is concluded that nano-SiO$_2$ additive can reduce the shrinkage tendency of polysiloxane effectively. Similar morphology has already been found on other hybrid coatings[15]. When exposed to VUV-AO or AO+VUV, the hybrid coating displayed essentially the same characteristics of a nano-particle dense surface (not shown here for brevity). In order to further distinguish the surface characteristics of the hybrid coating after exposure in AO containing environments, AFM investigation was conducted. Figure 5(a) shows the AFM images. Before exposure, the surface of the hybrid coating was smooth and defect free. Through analysis of the surface undulation of AFM image, the corresponding surface roughness was determined to be 5.14 μm^{-2}. After exposed to AO (Fig. 5(b)), AO+VUV (Fig. 5(c)), and VUV-AO (Fig. 5(d)), the coating surface became rough, and the corresponding roughness was 12.7, 12.6, and 15.6 μm^{-2}. Although the coating experienced greater mass loss during AO+VUV exposure than that during single AO exposure, it displayed almost the same surface roughness. After VUV-AO exposure, the coating displayed the most obvious surface roughness although it had the lowest mass loss.

3.2.3 XPS analysis

The surface composition obtained by XPS analy-

Table 2 Surface composition obtained by XPS analysis for the polysiloxane/SiO$_2$ (20 wt pct) coating before and after exposure in different conditions

Conditions	O/at. pct	C/at. pct	Si/at. pct	O/Si ratio
Unexposed	20.17	63.56	16.27	1.25
AO	54.22	19.17	26.21	2.07
VUV-AO	52.04	22.36	25.60	2.03
AO+VUV	54.79	22.92	22.29	2.46
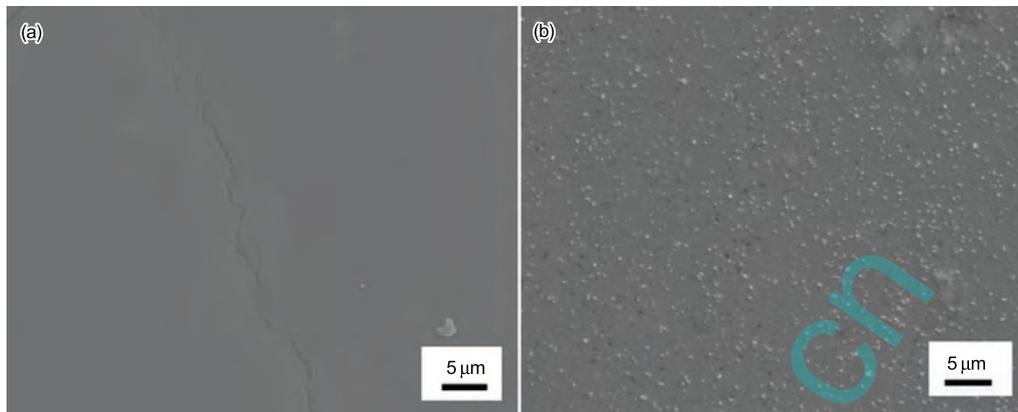
Fig. 4 SEM images of pure polysiloxane (a) and the polysiloxane/SiO$_2$ coating (b) after AO exposure
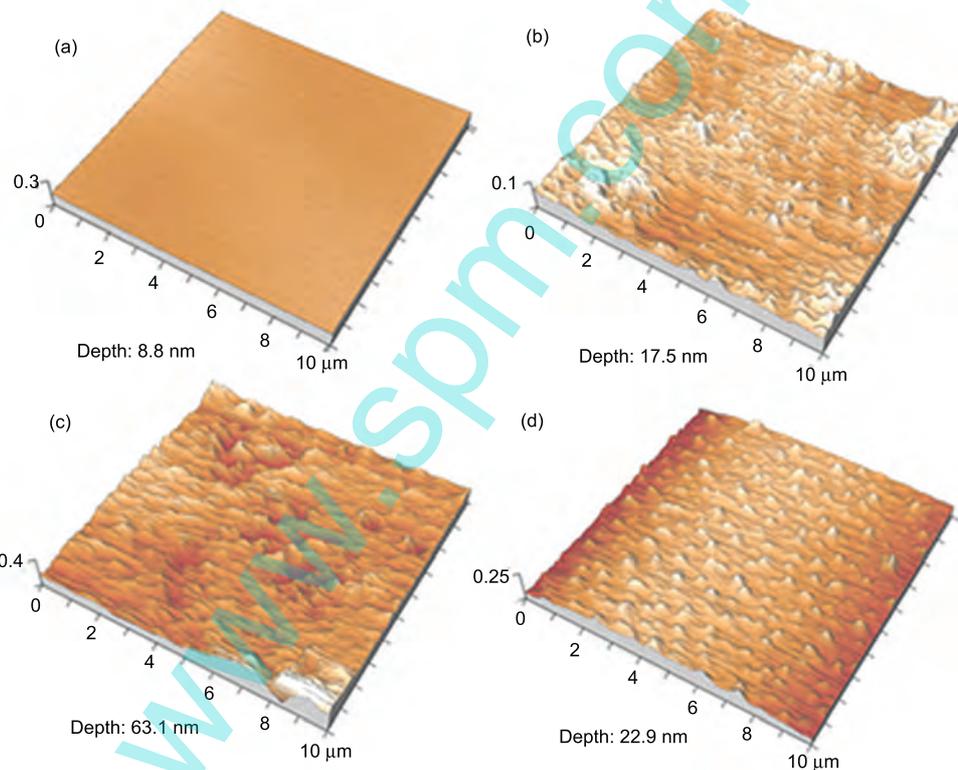
Fig. 5 AFM images from 10 μm×10 μm area of the polysiloxane/20 wt pct SiO$_2$ hybrid coating: (a) unexposed (Z scale is 300 nm), (b) exposed to AO (Z scale is 100 nm), (c) exposed to AO + VUV (Z scale is 400 nm), (d) pre-exposed to VUV for 1 h, then exposed to AO (Z scale is 250 nm)

sis of the polysiloxane/SiO$_2$ (20 wt pct) coating before and after exposure in different conditions is displayed in Table 2. As can be seen from the XPS results, the C content was 63.56 at. pct on the pristine surface. After AO and AO+VUV exposure, the concentration of C decreased to 19.17 at. pct and 22.92 at. pct, and the value of O-to-Si ratio increased from 1.25 to 2.07 and 2.46, respectively. During exposure, the hybrid coating interacted with incident AO beam, and the

organic parts of the hybrid coating were oxidized. It should be pointed out that the hybrid coating surface displayed higher C concentration after VUV-AO and AO+VUV exposure than that after single AO exposure, $i.e.$, VUV radiation could affect the process of AO erosion.

High-resolution XPS spectra of Si2p were performed to examine chemical bonding states of the exposed surface. As shown in Fig. 6, the XPS peak
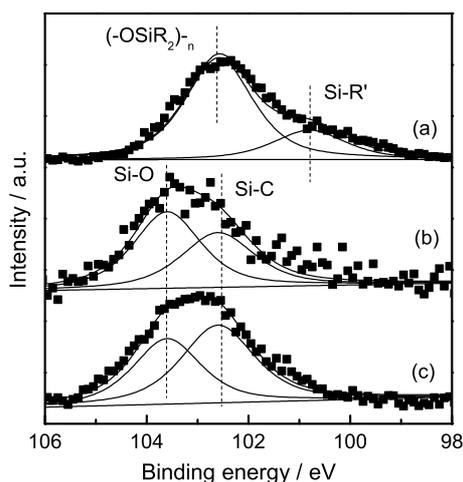
Fig. 6 High-resolution XPS spectra of Si2p of the polysiloxane/SiO$_2$ hybrid coating before (a) and after AO (b) AO+VUV (c) exposures

of Si2p could be separated into two Gaussian peaks. The two peaks assigned to -(OSiR$_2$)- and Si-R′ (R, R′ is CH$_3$, C$_2$H$_5$, etc.) bonds vanished after AO and AO+VUV exposures. This suggests that organic parts of the hybrid coating were oxidized by interaction with incident oxygen atoms[15]. According to tentative assignment, the photoelectron peak of the exposed surface consisted of two components centered at 103.3 and 102.4 eV, which corresponded to Si–O bonds and Si–C bonds, respectively. The Si–O signal (around 103.3 eV) could be interpreted as SiO$_2$[16], which is consistent with the O/Si ratio (see Table 2). Si–C bonds were assigned to the oxidized organic structures. After AO+VUV exposure, the surface displayed higher intensity of Si–C bonds compared to that after single AO exposure. Therefore, it is reasonable to propose that more organic parts of the hybrid coating were eroded by incident AO beam.

3.3 Synergistic effects of AO and VUV

According to the results of exposure tests, we have known that the polysiloxane/SiO$_2$ hybrid coating exhibits better AO resistance than pure polysiloxane coating, because SiO$_2$ nano-particles in the hybrid coating can decrease the reactive surface area of the hybrid coating. Besides that, the polysiloxane/SiO$_2$ hybrid coating presents different AO erosion characteristics in AO, VUV-AO, and AO+VUV exposure. The mass loss of the hybrid coating increases in the order of VUV-AO>AO>AO+VUV exposure. At the initial stage of AO exposure, organic parts of the hybrid coating were oxidized by incident AO beam, and its mass loss increased rapidly. With the erosion process, the coating surface became richer and richer in SiO$_2$. Once an entire SiO$_2$-rich layer formed, which can retard inward diffusion of oxygen effectively, the mass loss of the hybrid coating increased at a very small rate. In VUV-AO exposure, VUV pre-radiation could break those chemical bonds with low binding energy (such as C–H, Si–CH$_3$ bonds) and result in the formation of a great number of Si species, which

possess relative lower AO erosion rate[17–19]. In the subsequent AO exposure, the erosion rate of the hybrid coating decreased due to the existed Si-species on the pre-radiated coating surface. In AO+VUV exposure, VUV radiation could also break chemical bonds with low binding energy, and created free radical sites in the hybrid coating[20,21]. The radical sites, once formed, can result in damage remains trapped within polymers, i.e., the photogeneration of radical species in polymer matrices can be the initial steps in the degradation process[19]. Therefore, in AO+VUV exposure, VUV radiation could accelerate the process of AO erosion, which is called by synergistic effects of AO and VUV[9,10,19]. As mentioned above, the hybrid coating encounters lower AO erosion in VUV-AO exposure than that in single AO or AO+VUV exposure. Less of the SiO$_2$ nano-particles flake off due to oxidation of the surrounding organic parts, which may result in higher surface roughness.

4. Conclusions

In this work, the polysiloxane/SiO$_2$ hybrid coatings have been prepared on Kapton substrate by a sol-gel process. The erosion resistance of polysiloxane/SiO$_2$ (20 wt pct) hybrid coating was investigated by AO/VUV exposure tests in a ground-based simulation facility. Through the experimental studies, the following conclusions can be drawn:

(1) The E_y of the polysiloxane/SiO$_2$ hybrid coating is about 10^{-27} cm^3/atom, being one or two orders of magnitude lower than that of pure polysiloxane.

(2) During AO+VUV exposure, the value of E_y increases by 39% compared with that suffered from single AO exposure. Synergistic effects of AO and VUV are demonstrated.

(3) VUV radiation exhibits different characters whether it is combined with AO or not. It accelerates the erosion of the hybrid coating only when it is combined with AO beam.

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